

THE CHEMICAL EFFECT OF THE SPECTRUM.

BY

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[*Reprinted from the "Photographic Journal," 1881 and 1882.*]

LONDON :
HARRISON AND SONS, 59, PALL MALL.

1883.

Price Two Shillings.

HARRISON AND SONS,
PRINTERS IN ORDINARY TO HER MAJESTY,
ST. MARTIN'S LANE, LONDON.

TRANSLATOR'S PREFACE.

THE original of this small book is in German, but it subsequently appeared in French, and from a copy of the latter, annotated by the Author, it was translated for the pages of the *Photographic Journal*. The author, Dr. Eder, who is so well known for his practical and scientific acquaintance with photography, has in this work shown the depth of his knowledge of the photographic literature of every country; for the size of the compilation can by no means be taken as a measure of the labour it involved. Its value as a book of reference can scarcely be overrated, and it is for this reason that it has been deemed advisable to reprint it from the *Photographic Journal*. From some of the conclusions which the Author draws, the Translator and Editor has ventured to differ, but as to the facts there is no difference of opinion between them.

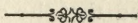
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November, 1883.

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CHAPTER I.

INTRODUCTORY.

FOR nearly half a century detailed experiments have been made on the chemical action of luminous rays. These experiments are very delicate, and the reactions which produce them extremely difficult to render useful; for not only the quality of the chemical agents used, but also the quality of light which acts upon them and causes the reaction has to be taken into account.

It is interesting to see in so many years how much has produced conclusive results. It is altogether impossible to deny that modern photo-chemists are those who, by aid of spectrum analysis, have explained the chemical reactions produced by light.

Of all the chemical compounds the salts of silver have been most studied in regard to their behaviour in light. It is upon these salts the observation was first made, that all rays of the spectrum have not the same chemical action. For this reason we shall first occupy ourselves with the action of the solar spectrum on the different silver-compounds, as they are, above others, those which occupy the chief position in photography.

Nearly all the salts of silver take a deep colour when exposed

to the action of white light, and for nearly all the blue and violet rays have a more intense reducing action than the red rays. In 1777 SCHEELÉ had already written, in his work "Von der Luft und der Erde," that of all the rays of the spectrum the violet most blacken silver chloride.

SENNEBIER, repeating Scheele's experiments, found that chloride of silver was darkened by violet light in 15 seconds in the same manner as if exposed to the yellow rays for $5\frac{1}{2}$ minutes, or during 20 minutes to the red rays.

BERARD (Gilbert, "Annales de Physique," 1813, vol. vi) and SEEBECK (Goethe, "De la Science des Couleurs," 1820, vol. ii, fig. 716) confirmed these experiments at the commencement of this century, and remarked that the extreme limit of the violet has the most intense chemical action. They impregnated paper with silver chloride, exposed it to the solar spectrum, and saw that the violet region strongly blackened it, the blue less, the yellow very little, or not at all, and the red very feebly.

Berard made another very interesting experiment. He collected by means of a lens the rays of the spectrum between the violet and the green, to form a beam of white light, and he proceeded in the same way to produce a brilliant white point by collecting the rays between the yellow and the red :* despite the heat of this beam, it had no action on silver chloride, although the exposure was prolonged for two hours. The other beam, although less intense, blackened silver chloride in ten minutes.

On the 22nd February, 1801, RITTER ("Des Rayons Lumineux Chimiques," Gilbert, "Ann. de Phys.," vol. vii, p. 525, vol. xii, p. 409) found that silver chloride was quickly darkened also by the rays which lay beyond the violet of the solar spectrum. He deduced from this that there were two kinds of invisible rays in the solar spectrum, the one below the red (where is found, as is known, the invisible-heat rays†),

[* There seems to be some mistake regarding the colour of brilliant dots produced. Yellow and red will never make white, neither will violet, blue, and green.—*Editor.*]

[† This term is that which is usually adopted ; but it must be remembered that rays are neither "heat rays" nor "chemical rays." The same rays may have a heating effect or a chemical effect, according to the kind of matter on which they fall.—*Editor.*]

the others beyond the violet possessing above all chemical properties. WOLLASTON ("De certains Effets Chimiques de la Lumière," Gilbert, "Ann. de Phys.," vol. xxxix, p. 291) confirms Ritter's deductions. It is recognised that solar light contains numberless rays completely invisible, which nevertheless well show their action on a photographic plate.

It is better to submit the substances to be experimented upon to the action of each region separately. Experiments made with pure spectrum colours—that is to say, colours produced through the decomposition of white light by means of a prism—are more exact than those made by means of variously coloured glasses. Light coloured by its passage through differently coloured glasses, like the spectrum colours, shows a totally different chemical action according to the colour of the glass through which it has passed; and this Seebeck had already indicated. He found that silver chloride darkened under the action of light, after having passed through violet, blue, and green-blue glasses, whilst it preserved its colour after passing through yellow, green, and red glasses. Other yellow substances take away the blackening property of sun-light: thus silver-chloride paper remains unaltered by light when it passes through chromate of potash,* sulphide of ammonium, the chlorides of iron, gold, and platinum (Draper, "Phil. Mag.," vol. xvi, p. 81). BECQUEREL, in his interesting Memoir ("Ann. de Chim. et de Phys.," 1843, vol. ix), made very curious observations upon the use of coloured glasses. He examined the rays which these glasses transmitted, and remarked that the light so obtained was not homogeneous when examined by the spectroscope; and that for this reason it was useful to try coloured glasses in the spectroscope before adopting them for photographic experiments.

As the blue and violet light of the extremity of the spectrum

* In 1855 Hunt recommended a mixture of bichromate of potash and gum or glue for tinting the windows of the dark-room in which sensitive plates have to be prepared (Hunt's "Photography"). I cannot recommend this preparation, because mixtures of this kind become brown or green under the action of light, and are then not so safe. For the action of other colouring matters, and particularly organic matters, see Burdy, "Bulletin de la Société Française," 1879, p. 98; Abney, Tóth, and Eder, "Photographic Journal," 1879.

has the most considerable reducing effect on most compounds, for a long time, in fact since the discovery of photography, photographic laboratories have been glazed with yellow or red glass; this light, it is true, does not act upon the usual photographic preparations, and it is for this reason that it is customary to consider this light as non-actinic.

All rays of the spectrum, then, have not the same chemical energy; and on different compounds the decomposing action by various colours is also variable.

The closely allied haloid compounds of silver, under the influence of coloured rays, exhibit decompositions which are very diverse in character. This was first indicated by Sir John Herschel in 1840, and minutely described by Robert Hunt, in his very complete work ("Researches on Light," 1840), as regards daguerreotype plates. The influence of the spectrum upon wet-collodion plates was first investigated by J. Müller (Pogg., vol. lxvii, p. 133). He caused spectra to be photographed by Haasé, at Fribourg. He remarked that it was only the region of the spectrum above G which was impressed on the plate. The plate also showed an impression of the fluorescent spectrum far beyond the ordinary visible spectrum. A wet-collodion plate, exposed during fifteen seconds, showed a spectrum with all the Fraunhofer lines from G as far as the group P, which STOKES had observed by means of fluorescence. The rays H, L, M, N, and O appeared exactly as in Stokes's spectrum, observed by means of quinine, which is a proof that the same rays which can produce fluorescence can also act upon sensitive salts of silver. In 1857 HELMHOLTZ presented, at a meeting of the Société du Bas Rhin, at Bonn, some very successful photographs of the ultra-violet end of the spectrum. Since then, the solar spectrum has often been photographed. RUTHERFORD, of New York, has photographed a spectrum 2.50 metres long, in fifteen separate pieces. The spectra of gases, &c., have also been photographed.

The material of the prism, by means of which the solar light is decomposed, is not without influence on the separation of the rays themselves in the spectrum. At first it was considered as a matter of indifference as to the kind of glass which formed the prisms, since it was believed that each coloured region would have the same relative action. Thus it

was that Herschel, ordinarily so conscientious, has not noted anywhere the density of the glass of his prism, with which he discovered the greatest heating intensity of the spectrum to be the infra-red rays.

SEEBECK had already worked in this direction from 1806 to 1808, and it was only in 1819, through his works published in the *Journal of the Berlin Academy of Science*, that he made known his experiments as to the differences obtained when using glass of different compositions. Since then, this question has been much studied.

Further, the atmospheric constitution of the sky influences the results obtained. H. W. VOGEL has shown that the chemical intensity of the solar spectrum, on account of the variable transparency of the atmosphere, is subject to very considerable fluctuations. Thus, the maximum of intensity for the reduction of silver chloride is sometimes found in the ultra-violet and sometimes in the violet, and often even in the blue,—even when employing pure silver salts.

It is curious that these compounds of silver behave differently to light, according to the manner in which it acts,—that is, according as they are allowed to darken spontaneously, or as their colour is developed. The nature of the development has also a considerable influence (mercury, sulphate of iron, pyrogalllic acid, &c.).* To produce an image by development, it is necessary to give a shorter exposure than if an image is to be obtained without development. This is true for all colours of the spectrum with which it may be desired to obtain an image on the salts of silver.

* The latent image can be developed by salts of uranium (Van Monckhoven), by glucosides, sugar, organic salts of iron, resins, ethereal oils, organic bases (Carey Lea, "*British Journal of Photography*," No. 849). Relatively to the spectrum, these developers have not yet been experimented with.

CHAPTER II.

ACTION OF LIGHT ON SILVER SALTS.

WE now give in detail the effect of the action of coloured light on each salt of silver.

SILVER NITRATE, in a pure state, or in an aqueous solution (without contact with organic matter), is insensitive to light. With organic substances, such as albumen, gum, paper, &c., it blackens rapidly in blue light, whilst red light has no effect on it. Paper impregnated with silver nitrate blackens when exposed to the solar spectrum, from the violet to the yellow. Wedgwood remarked in 1802, that nitrate of silver paper is only very feebly attacked by the red rays; the green and the yellow rays do possess darkening power, but the most intense and rapid effects are found in the blue and violet (*"Ann. de Phys.,"* vol. xiii, p. 113). Under the action of the rays coming from the blue region of the spectrum the paper takes a blue-brown tint, whilst the violet rays give a peculiar rose-colour. The rays of minimum activity are found in the middle of the yellow; the maximum, in the middle of the blue. From this point there is great diminution of activity to the limit of the violet. The ultra violet only darkens it very feebly (Herschel, *"Photographic News,"* 1859, vol. iii, p. 2).

SILVER IODIDE.—If a paper impregnated with silver iodide is exposed to the rays of the solar spectrum, according to Herschel, an image is obtained from the red to the violet; the impressions produced by the violet go further with this compound than with silver bromide (*"Photographic News,"* vol. ii, p. 279). The silver iodide paper is most sensitive to the ultra-violet rays of the spectrum, the maximum of intensity depending on the quantity of free silver nitrate present. The effect commences at the middle of the red, where the paper takes

an ashy-grey tint, whilst under the action of the less refrangible rays it takes an orange tint. The action of the ultra-violet rays is shown further on the silver-iodide paper than on paper impregnated with the chloride or bromide of the same metal (Hunt's "Researches on Light").

The experiments which we have just described give an image directly visible to the eye without the aid of development. The action of light is quite another thing when, after once being impressed, the image is brought out by a developer. Daguerreotype plates, with silver iodide developed by mercury, only show a very feeble sensitiveness to red light; they are, nevertheless, coloured slightly rose. Herschel and Hunt did not find any activity in the yellow and orange, and in the green the action was scarcely distinguishable. The blue and the violet rays had, on the other hand, a very intense action on these plates. The maximum action was found between G and H, extending from the ultra violet as far as F (Becquerel). When sufficiently long exposure was given (Draper), or when the silver-iodide plate was exposed to diffused light before exposure, the spectrum from the red to the ultra-violet was impressed in a very appreciable manner (Becquerel, "La Lumière," p. 891).

Films of silver iodide developed with pyrogallic acid are not at all, or very little, influenced by the red; in the orange, the yellow, and the green they do not change, according to Crookes, even after a very long exposure; in the blue, and in the region beyond, they are strongly affected. If they are exposed for a longer time than is necessary for the blue and violet rays to have their proper action, there is "solarization,"* though it is not apparent in the yellow, orange, or red. The place of maximum action is found in the indigo and the commencement of the violet. Monckhoven found that silver iodide was sensitive to the limit of the violet.

Schulz-Sellack ("Berliner Berichte," vol. iv, p. 210) has stated that a plate prepared in the ordinary manner with iodized collo-

* If salts of silver are exposed for a long period to light, their power of giving an image by a developer increases up to a certain limit. After a very prolonged exposure this intensity decreases, the image becomes feeble, and scarcely shows itself on development. This phenomenon goes under the name of solarization.

dion (viz, by coating a glass plate with iodized collodion, immersing it in the silver-nitrate bath), and developing with ferrous sulphate, is sensitive to the rays of the spectrum from the ultra violet as far as G. Becquerel states the same thing ("La Lumière," p. 87).

Vögel has remarked that the chemical action of the different colours of the spectrum is totally different. It differs accordingly as pure salts of silver are applied, with the addition of silver nitrate or an organic sensitizer. The sensitiveness towards the red then increases in a notable degree. Collodion iodized with cadmium iodide was sensitized in a silver bath; after having been washed, the plate was dried; the plates thus prepared were exposed, and, after well washing, dried, and the development carried out by ferrous sulphate acidified with citric acid to which was added silver nitrate: silver bromide and chloride were also used, but in that case the development was carried out by an ammoniacal solution of pyrogalllic acid with the addition of potassium bromide.

Dry silver iodide of this kind was found sensitive from H to D, sometimes even to A. The maximum of sensitiveness was found between G and F. Silver iodide in the wet state is less sensitive in the green. The manner in which silver iodide behaves when exposed to light with free silver nitrate is very remarkable. Its sensitiveness increases from the ultra violet to G, where it attains its maximum, and there it abruptly falls. (This is according to Becquerel.) Silver iodide thus shows its maximum of sensitiveness in the blue-indigo part of the spectrum.

When the exposure is sufficiently prolonged, silver iodide is sensitive to all the colours of the spectrum as far as A in the red ("Pogg. Ann.," vol. cl, p. 453).

SILVER BROMIDE.—Silver bromide discolours as a general rule more rapidly than the iodide of the same metal. A small quantity of free silver nitrate aids its decomposition by light, but nevertheless not so markedly as it does the iodide.

Silver bromide on paper with an excess of silver nitrate prepared by double decomposition is acted on by the spectrum as far as the extreme visible part of the red. The maximum intensity is found in the indigo (Herschel). The

effect reaches from H to F; if, however, a preliminary exposure to diffused light is given to the paper for a short time, it blackens under the influence of the spectrum as far as the red (Becquerel, "La Lumière," p. 86).

Daguerreotype plates sensitized with bromine and developed with mercury are more sensitive to the green than those sensitized with iodine. It is for this reason that, in 1840 and 1842, Hunt recommended the use of the former ("Phil. Trans."). He said on this subject, "That a new photography ought to be created, the foundation stone of which would be bromine." As a matter of fact, daguerreotype plates were produced with bromo-iodide of silver; chlorine was also often employed.

Wet-collodion plates with silver bromide, with excess of silver nitrate, developed by pyrogallic acid, are infinitely less sensitive to white light than if prepared with iodide, and the images obtained have very little vigour; on the other hand, green is admirably reproduced (Herschel). William Crookes had observed this action, and indicated that it was produced from E and F as far as H in the violet. Schultz-Sellack found that the bromide of silver, with excess of silver nitrate (prepared and developed as we have shown before when speaking of the iodide), is sensitive to near F in the blue; Becquerel found as the limit the line E ("La Lumière," p. 86).

According to Dr. H. W. Vogel ("Phot. Corr.," vol. x, p. 212), silver bromide prepared in a wet-collodion plate (and with excess of silver nitrate) is particularly sensitive to the more refracted rays in the blue of the visible spectrum when development takes place by acid ferrous sulphate; on the other hand, silver bromide in a collodion dry plate (obtained by washing and drying ordinary wet plates) shows a greater range of sensitiveness to colour, and it is impressed by the rays as far as D in the orange, and even into the infra red. The presence of silver nitrate intensifies the action of the blue and the green rays. When sufficiently long exposure is given to pure dry bromide of silver in a collodion film it is sensitive to the extreme red, in such a way that the line A is quite distinctly seen; even a part of the infra-red region is taken—a part which equals in length the distance of B from A ("Berliner Berichte," vol. viii, p. 1635). Alkaline develop-

ment with pyrogallic acid causes greater sensitiveness to red light.*

Silver bromide prepared with an excess of soluble bromide with gelatine, with a sufficiently long exposure, according to Monckhoven, gives an image from the ultra violet into the red. The blue and the violet rays have the strongest effect; the red, on the other hand, the least. He has also remarked that freshly made silver-bromide emulsion is orange by transmitted light, and that its sensitiveness extends from the ray F as far as M. Old and ripened emulsion, in which the silver bromide is molecularly changed, appears blue by transmitted light, and its sensitiveness extends as far as A in the red. Very old green emulsion is even sensitive as far as the infra-red rays. (*See further, for the sensitizing influence of gelatine.*)

SILVER CHLORIDE.—Pure silver chloride is chiefly changed and blackened in the regions which extend from the blue to the ultra-violet. Silver-chloride paper containing an excess of silver nitrate blackens first in the ultra-violet, then between the rays H and G, and, lastly, in the blue as far as the ray F. If silver chloride has been exposed beforehand for a few moments to the light (without, however, the time of exposure being enough to allow a visible impression of the light), it blackens as far as the infra red, according to the experiments of Seebeck, Herschel, Poitevin, Zenker, and others. On paper treated like this we find two places where the light has acted most vigorously—one situated between the rays G and H, the other between D and E (Becquerel, "*La Lumière*," p. 84). H. W. Vogel gives the following explanation of this phenomenon ("*Pogg. Ann.*," vol. cxxxv, p. 284). He says that silver chloride, having taken a violet tone by the light, acquires thereby the faculty of absorbing more strongly the yellow and orange rays of the spectrum, in such a manner that the rays which at first appeared inactive become by that means active. It may be said that in the process with silver chloride, that photographers daily employ, it is the violet and ultra-violet rays which are particularly active. The same thing is observed in Bunsen and Roscoe's actinometer, in

* Upon the influence of the molecular structure of silver bromide as to its sensitiveness to colour, *see* subsequent pages.

which chloride of silver paper is employed for their pendulum photometer.*

Silver chloride mixed with collodion, with an excess of silver nitrate (and with development), is sensitive from the ultra violet rays as far as G. Dry collodio-chloride of silver shows after development, a blackening from the violet as far as the red, when the exposure has been sufficiently prolonged; with a very prolonged exposure the action extends as far as A. If it be employed for dry plates, it will be found to be much less sensitive to the light than silver bromide, and that it requires twice as long an exposure (Schultz-Sellack; H. W. Vogel; "Pogg. Ann.," vol. cliii, p. 223; Becquerel, "Phot. Mittheilungen," vol. xi, p. 182).

SILVER FLUORIDE is much less sensitive to the action of light than the chloride, bromide, or iodide of the same metal. It does not darken strongly when exposed to direct light, and does not give good latent images capable of being developed. According to Monckhoven, it is less sensitive to the ultra-violet than the iodide and bromide, whilst, on the other hand, it is more sensitive to the yellow and green regions.

A MIXTURE OF SILVER IODIDE, BROMIDE, AND CHLORIDE ordinarily unite the qualities of each of its elements; so that a product of this kind ordinarily gives a qualitative and quantitative sensitiveness greater than each of its factors separately. It is for this reason that a mixture of this kind is used in photography.

When daguerreotype plates are sensitized by a mixture of bromine and iodine, or iodine and chlorine, they give the spectrum from the ultra violet (the same as silver iodide alone) as far as the infra-red. The maximum intensity is situated between the rays G and H (Becquerel, "La Lumière," vol. ii., p. 91). For this reason in the practice of daguerrotype the use of iodide alone was soon abandoned, and the plates were sensitized by iodo-bromine or iodo-bromo-chlorine, and much superior results were obtained to those which were got by the first method.

* The time necessary to produce an exactly determined discoloration is proportional to the chemical intensity of the light (*see* Bunsen and Roscoe, "Phil. Trans.").

In the wet-collodion process silver bromo-iodide is almost exclusively employed (in presence of an excess of silver nitrate, and acid development by ferrous sulphate). This mixture is more sensitive than each of the two elements taken separately (Carey Lea, "Brit. Journ.," 1875). Müller and Schultz-Sellack have shown that the sensitiveness of the silver bromo-iodide extends further from the violet region towards the red than silver iodide does by itself. The last of these two *savants* found that films of bromo-iodide reached in sensitiveness from the ultra-violet as far as the ray E in the green. Thus the sensitiveness to colour is more considerable in a mixture of iodide and bromide than in each of the two salts taken separately. According to H. W. Vogel, silver bromo-iodide, mixed with collodion in presence of an excess of silver nitrate, is sensitive as far as the ray D when developed with acid ferrous sulphate. Its maximum of sensitiveness is situated about the line G: under the same circumstances, when the iodide is greater in quantity than the bromide, it is remarked that the ultra-violet and violet regions are chiefly impressed on the bromo-iodide; on the other hand, when the bromide has the preponderance, the light blue and green regions give the maximum intensity.

Pure and dry silver bromo-iodide is less sensitive in the ultra violet and in the green than when it is wet (in presence of silver nitrate), and is in general much less modified by the action of light.

CHAPTER III.

PHOTOGRAPHS IN NATURAL COLOURS.

WHILST silver iodide or bromide, whether directly printed upon in the spectrum or if the latent image is developed, shows an impression by a blackening more or less intense, and never gives a coloured image, it is nevertheless possible with silver chloride to reproduce natural colours. Dr. Seebeck, of Jena, was the first who in 1810 obtained a reproduction of a spectrum in natural colours on chloride of silver paper. In the "Farbenlehre" of Goethe, he says (*see* also Dr. Roth, "Fortschritte der Photographie," 1868, p. 20), "When I project a spectrum, produced by a prism correctly constructed, upon moist chloride of silver paper, and if I continue the printing for fifteen to twenty minutes, giving a constant position to the spectrum by any means, I observe as follows:—In the violet band the chloride is a reddish brown (sometimes more violet, sometimes more blue), and this coloration extends well beyond the limit of the violet, though it is not stronger than in the violet; in the blue band the chloride takes a clear blue tint, which fades out, becoming lighter in the green. In the yellow I usually found that the chloride was intact; sometimes, however, it had a light yellow tint; in the red, and beyond the red it took a rose or lilac tint.

"This image of the spectrum shows, beyond the red and the violet, a region more or less light and uncoloured; this is how the decomposition of the silver chloride is seen in this region. Beyond the brown band, of which we have written above, and which was produced in the violet region

and beyond, the silver chloride was coloured a grey-violet for a distance of several inches. In proportion as the distance from the violet increased, the tint became lighter. Beyond the red, on the contrary, the chloride took a feeble red tint for a considerable distance. When wet silver chloride, having received the action of light for an equal time, is exposed, the blue and violet behave as above. In the yellow and red regions, on the other hand, it is found that the silver chloride becomes lighter; and although this phenomenon is not very intense, it is nevertheless quite visible, and cannot be mistaken. The same can be remarked as in the preceding case: the part acted on by the red rays, and by those beyond, take a light red coloration."

Thus wrote Dr. Seebeck in 1810. There was, therefore, nothing new in the communication made in 1839 by Sir J. Herschel ("Athenæum," No. 621), that is to say, that when chloride of silver paper, which was preliminarily darkened in light, was exposed to the spectrum, the paper took tints analogous to red, green, and blue.

In 1848 the French physicist, Edmond Becquerel, succeeded in reproducing upon a daguerreotype plate not only all the colours of the spectrum, but also, up to a certain point, the colours of drawings and of certain objects. Niépce pursued the subject, and the colours which he obtained were much more intense and vivid than those obtained by his predecessor.

When a silver plate, properly polished, is covered with a thin film of chloride of the same metal, this film is altered under the influence of the spectrum, showing natural colours. The silver plate may be chlorinated in different ways; but then the results obtained differ. A silver plate is immersed in a solution of ferric chloride or cupric chloride (Becquerel), or in a mixture of two solutions—one potassium chloride and the other cupric sulphate. It is then washed and dried (Niépce de St. Victor, "Comptes Rend.," vol. xxxi, p. 491). It may also be immersed in chlorine water till it takes a feeble white rose tint (Becquerel).

Becquerel preferred voltaic chlorination. He operated thus:—The silver plate, taking the place of the positive pole, is immersed in a solution of 12·4 per cent. of hydrochloric acid in water; the negative pole is formed of a platinum plate.

At the end of a minute it takes successively a grey, yellowish, violet, and blue tint, which are again repeated in the same order. The moment that the violet coloration begins to appear for the second time, the operation is suspended the plate is washed, and dried over the flame of a spirit lamp. The silver plate thus prepared reproduces all the colours of the spectrum. The blue and the violet are reproduced with the greatest intensity; the green is only feebly shown. If the plate is warmed to 100° C., which gives the film a rose-colour, the sensitiveness is particularly increased for the yellow region.

(More precise directions can be found in the account given by Becquerel in the Séance of the Société Photographique de Paris on the 18th December, 1857, and in Dingler's "Polytechnischen Journal," vol. cxxxiv, p. 123.)

The sensitiveness of the film of silver chloride to coloured light depends on its thickness and on the concentration of the chlorinating solution, but still more on the purity of the silver, which ought not to contain more than 10 per cent. of copper (Nièpce, Martin, "Handbuch der Photographie," 1857, p. 311, 1st and 2nd parts). The chloride of copper gives to the colours a greater vividness than chlorine-water alone. The use of very dilute chlorine is favourable to the reproduction of the yellow region; very concentrated chlorine gives, on the other hand, the orange and the red with great intensity. The employment of a mixture of magnesium chloride and of cupric sulphate is to be recommended.

At a later date, Nièpce chlorized by means of calcium chloride. This alkaline bath did not give such constant results as the chlorinating bath previously used by Becquerel (*see above*); this method is, however, very simple. The sensitiveness of a prepared silver plate is strongly exalted if it is treated, before exposure, with a saturated solution of lead chloride in dextrine (4th Memoir, "Comp. Rend.," 1862, vol. liv, p. 281).

Upon films of this description positive pictures are always obtained; that is to say, the black lines of a copper plate engraving are reproduced in black (*loc. cit.*, p. 299).

Sometimes coloured images are obtained on collodion films containing silver chloride. The colours appeared after fixing

with potassium cyanide, and when the vapour of chloride of iodine is allowed to act ("Bulletin de la Société Française," 1857, p. 116). Chloride of silver emulsion, with a slight excess of silver nitrate and citric acid, is coloured, as is known, a slate-coloured grey by the action of light: under a red glass it becomes red; under aniline green it becomes green (Simpson, "Photographic News").

Pure silver chloride upon paper becomes rapidly violet in the ultra-violet; but in the visible part of the spectrum it changes slowly; if it is given a preliminary exposure to diffused sunlight, so as to form violet subchloride, it gives the spectrum colours within the same limits. The yellow and green regions are, it is true, feeble and scarcely visible.

Silver chloride, in the presence of an excess of silver nitrate, blackens only in the ultra-violet; but, if exposed first to diffused light, it is also sensitive in the visible spectrum from the red to the blue; the colours appear only feebly, but can, however, be easily distinguished (Becquerel, "Phot. Archives," 1868, p. 300). By adding to it appropriate substances, *e.g.*, salts rich in oxygen, the violet silver chloride gives upon paper much better images.

Poitevin prepares ordinary photographic paper, first with a layer of silver chloride by floating it upon a solution of sodium chloride, and after upon a solution of silver nitrate. After having washed the excess of nitrate, the paper is immersed in a very dilute solution of stannic chloride; the bath and its contents are exposed for five or six minutes to diffused light; the paper is taken out, and well washed, to increase the sensitiveness of the silver subchloride thus formed upon the paper, it is then treated with a solution of potassium bichromate and cupric sulphate. The sheets of paper, dried in darkness and exposed under coloured pictures on glass or in an enlarging apparatus, gave coloured images which could be fixed by sulphuric acid (De Roth, "Fortschritte der Phot.," 1868, p. 22; "Comptes Rendus," 1868, vol. lxi, p. 11).

Later, St. Florent specially occupied himself in experiments tending to reproduce the spectrum colours by means of silver chloride ("Bulletin de la Société Française," 1874). Chloride of silver paper is prepared by him in the following manner:

—He immerses ordinary or albumenized paper in a solution of silver nitrate; he afterwards plunges it into a solution of uranium nitrate and zinc chloride in alcohol acidulated by hydrochloric acid; the paper is then exposed to light till it takes a violet-blue or lavender tint. Before exposure, the paper is sensitized in an acid solution of mercury nitrate, and it is more or less dried on blotting-paper. Under the action of light the mercuric chloride which is formed by this immersion is transformed into mercurous chloride and chlorine, which transforms the subchloride of silver into white-silver chloride, and at the same time takes up such a particular physical constitution as to render it capable of taking impressions of the luminous coloured rays. When the silver chloride is placed in concentrated nitric acid, it is coloured when exposed beneath a coloured negative. It is to be noted, however, that all the colours appear mixed up, from the red to the violet, which is probably due to the preponderating influence of the infra-red and ultra-violet rays. If collodion is used to retain the silver chloride, a helio-chromograph upon glass can be obtained.

The nature of the chloride, that is to say, of the metal with which the chlorine is combined, influences so much the quality of the silver chloride obtained by its action, that the action of light altogether varies according to the metallic chloride employed. This influence has already been remarked upon in speaking of the reproduction of colours by means of the silver subchloride: the same remarks also hold good when bromide and iodide of silver are used for photography by development.

Thus according to the nature of the chloride employed to precipitate the silver chloride, and according to the coloration of the different glasses to the action by which it is submitted, so does it take different colorations. This is a curious and remarkable fact, for it cannot be that silver chloride is affected in its properties by a small quantity of nitrate (formed from the double decomposition of the soluble chloride and the silver nitrate) which is indifferent to light, and that it is only mixed with it by the fact of preparation. Hunt had already observed this phenomenon: he soaked different papers, impregnated with the chlorides of different metals, in a solution

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of silver nitrate, and exposed them to the light under glasses of different colours.

Chloride employed to form Silver Chloride.	Coloration produced by the action of Light beneath.			
	Blue Glass.	Green Glass.	Yellow Glass.	Red Glass.
Ammonium chloride	Olive brown	Light brown	Brown ...	Deep orange.
Potassium ..	Light purple	Sky blue ...	Light violet	Red.
Sodium ..	Purple ...	Blue	Violet ...	Red brown.
Barium ..	Purple ...	Lilac	Red brown	Light red.
Calcium ..	Intense violet	Light blue...	Blue	Ruddy.
Manganese ..	Intense brown	Ruddy ...	Light rose...	Yellow.
Ferrous ..	Red... ..	Uncoloured	Light red ...	Lead colour.
Ferric ..	Blue ...	Yellowish...	Straw colour	Yellowish green.

If these papers were darkened in direct solar light, or under coloured glasses, the following colorations were obtained :—

	Coloration produced by the action of Light.				
	White.	Blue.	Deep green.	Yellow.	Red.
Ammonium chloride	Red brown	Olive green	Deep green	Dirty yellow	Red.
Barium chloride ...	Deep brown	Deep brown	Dirty ...	Green brown	Red.
Chlorine water ...	Rich brown	Blue black	Black ...	Deeper brown	Deep red.
Potassium chloride	Greenish brown	Brown black	Blacker	Bluish ..	Ruddy.

By prolonging the exposures, other colorations were obtained.

Bromide and iodide of silver behave in an analogous manner. These substances also show, in their decomposi-

tion by light, colorations which differ according to the kind of iodide or bromide which is used in their formation. I have before me a very old note by Zantedeschi, and by Bortinetto, dated 1856, "Compt. Rend.," vol. xxi., p. 243. This is what they say:—They made negatives by the ordinary collodion process, introducing different iodides, which they developed with pyrogallic acid. The different tones of the negatives were as follows:—

Iodide of silver obtained from potassium iodide—black.				
"	"	"	cadmium	" deep violet.
"	"	"	zinc	" { colour of
"	"	"	ammonium	" { light In-
"	"	"	iodo-hydrate of	" { dian ink.
			quinine	" { ruddy black.
				" { purple red.

Negative collodions containing iodides and bromides give, according to the metal in which the iodine or bromine is combined, negatives of different aspect—sometimes light, sometimes deep.

The manner of acting on the different bromides in the collodio-bromide emulsion process has been experimented upon by Warnerke ("Photographic Journal," February, 1876); his researches were only carried on with regard to white light. He found that the intensity of the images and the sensitiveness of the film differed according to the nature of the bromide. Zinc bromide, for example, gives images more intense than does copper, and gives a superior sensitiveness to that produced by other bromides. Collodio-bromide emulsions also discolour differently according to the kind of bromide used: silver bromide discolours blue, when bromides of uranium, ammonium, potassium, and sodium are employed to produce it; red, when bromides of cadmium and zinc; grey, when bromide of iron and bromine.

Niépce (Martin, "Handbuch der Photog.," 1857, p. 311) made some very curious observations tending to show the relationship existing between certain coloured flames and the photographic images produced by light. He immersed a plate of silver chloride in chlorine-water, to which he added a chloride capable of colouring a flame. The red of the solar spectrum

is particularly well reproduced upon plates of this kind when the chlorine-water, which is used to chlorinate it, contains strontium-chloride, which colours the flame purple red. By adding to the chlorine-water calcium-chloride or uranium-chloride, the reproduction of the orange region of the spectrum is helped for the yellow sodium-chloride. The green region is reproduced by the addition of boracic acid, nickel chloride, or a salt of copper. The blue can be obtained by ammoniacal copper chloride; and, finally, the violet by a mixture of strontium-chloride and copper sulphate.

Nièpce imagined that all the substances producing coloured flames should also give coloured images by light; and that all bodies which do not colour flame, do not give images which are coloured by light.

I only give these remarks to make this work as complete as possible; for experiments do not confirm them in any degree.

CHAPTER IV.

INFLUENCE OF THE DEVELOPER UPON THE SENSITIVENESS TO LIGHT OF THE HALOID SALTS OF SILVER.

THE direct action of light* is shown in its greatest intensity on silver chloride: it blackens under the influence of the luminous rays, especially in the presence of organic matter and silver nitrate with infinitely greater rapidity than do the bromide and iodide. For this reason it is employed where photographic images are to be obtained by the direct action of light, without using development (for example, in printing negatives with silver-chloride paper); on the other hand, the iodide and bromide are infinitely better for giving, with a very short exposure, a latent image, which can be developed by means of reducing agents. The latent action of light takes place much more rapidly; and when it is desired to obtain images in the minimum of time, it is useful to employ compounds giving a latent image which can be developed subsequently. For this reason, in modern processes (at least in processes for the production of negatives) silver iodide and bromide are sure to have a greater preponderance than chloride.

The old experiments of Herschel and Hunt showed that the relative sensitiveness of the compounds of silver vary with the mode of development adopted. The sensitiveness of salts of silver to light can be shown in three different ways.

* By the *direct action* of light, I mean the visible change which light produces when acting upon a body; for instance, the blackening of silver chloride by light,—the property that stuffs have of bleaching,—the oxidation of iron salts. If, on the other hand, it produces upon a sensitive film an invisible image, which leaves the film quite intact, but which favours decomposition by means of other agents, I call that phenomenon a *latent action*. Thus a photographic image is developed by mercury vapour, or the reducing salts of iron.

They can blacken visibly in the light (*direct action of light*), or give a latent image which can be developed by an acid developer or by an alkaline developer of pyrogallol.* The above two methods of development differ from one another altogether: whilst in the first method the image is formed almost entirely from free silver nitrate, which precipitates as reduced and finely divided metallic silver, depositing upon the parts altered by light, the silver iodide being unreduced; in the second, on the other hand, the silver nitrate is absent, and it is the bromide alone which, first acted on by the light, is afterwards reduced. Thus, in the first case, the parts acted upon by the light attract the nascent precipitated silver (silver precipitated by ferrous sulphate, for example); in the other, the same parts are attacked with the greatest ease by certain reducing agents.

We have already spoken of the difference which exists, 1st, between films of wet silver salts, that is to say, those which are treated with ferrous sulphate and the silver nitrate which is on the plate, and, 2nd, between the dry plates which can be developed either by iron and silver, or with alkaline pyrogallic acid. These two series of experiments cannot be compared, amongst themselves, with that which is to follow; for, to know the effect and power of the developer, pure and dry films of similar haloid salts of silver must be operated upon. These films ought to be developed in different ways, whilst in the above-described cases the haloid salts of silver were sometimes exposed pure, and sometimes in the presence of silver nitrate.

It can be said in general that alkaline development by pyrogallic acid, with the addition of potassium bromide, gives, of all known agents, the most intense impressions with the least exposure. This is quite as true for the violet rays as for the red rays: a very short exposure to white light can also be made apparent by the same method. On the other hand, alkaline development gives also the least active part of the spectrum, that is to say, the red, with greater intensity than

* To the developing substances indicated and studied by Carey Lea ("British Journal of Photography," 1877), the ferrous oxalate and lactate, which act very energetically on dry plates, and develop like the alkaline pyrogallic acid developer, can be added.

does development with acid and iron. In relation to this, I quote the experiments of H. W. Vogel, which, having been made only with white light, have more importance as regards the blue and violet rays than for the red and yellow rays.

H. W. Vogel ("Berliner Berichte," vol. vi, p. 88; "Photo. Corr.," vol. ix, p. 190) prepared emulsions with iodide, bromide, and chloride of silver, by adding to a collodion containing silver nitrate an iodide, a bromide, &c.; he added iodide in such a way as to have excess of silver nitrate, which he eliminated by washing in water after coating the plates with the emulsion: with these he prepared his dry plates. The wet-collodion plates were prepared in the ordinary manner, and contained excess of nitrate.

The following is the scale of sensitiveness resulting from his experiments. The most sensitive salt is named first:—

The wet process, acid development, for strong lights: silver iodide, bromo-iodide, bromide. For feeble light, shadows, or those which, by the absence of violet and indigo rays, are not completely white: bromo-iodide, iodide, bromide.

It is for this reason that, in practice, where details in the shadows are desired, a mixture of iodide and bromide of silver is desirable. Five atoms of iodide for 1 atom of bromide seem to be the best proportion (Vogel, "Photo. Mitt.," bk. lix, p. 239).

For alkaline development (pyrogalllic acid 1 : 200 and caustic potash), the nitrate having been eliminated by washing, either wet or dry: silver bromide, bromo-iodide, iodide.

When developing *with neutral pyrogalllic acid*, which acts, of course, very slowly: bromo-iodide, bromide, iodide.

When *pyrogalllic acid, slightly acidulated by acetic acid*, is used alone, it does not develop any image, but does so on the addition of silver nitrate.

The following is then the scale of sensitiveness:—silver bromo-iodide, iodide, and bromide.

It is also to be remarked that plates prepared with bromo-iodide of silver, which is very rich in bromide (1 atom of bromine to 1 of iodine), are more sensitive to acid development than those which are rich in iodide (1 atom of

bromine to 5 atoms of iodine). Development with acid pyrogalllic acid seems to give, in dry plates, more detail than development with acid iron. I have observed this fact myself on different occasions.

These observations are still more interesting, as it has been observed that a bromo-iodized collodion containing a large proportion of iodide is better for the ordinary wet process. For this reason Tóth and myself recommended, in 1876 ("Photo. Corr.," vol. xiii, p. 97), a collodion containing plenty of iodide for portraits and reproductions of drawings. This collodion has given excellent results. Vogel, Kleffel, and other German authors add to a negative collodion 3 or 4 parts of iodide to 1 part of bromide. It is necessary to add, however, that many foreign photographers, and particularly the English, use a collodion richer in bromide, as I remarked at the time ("Photo. Corr.," vol. xv, p. 204). Thus William Heighway adds 3 parts of bromide to the 5 of iodide which the collodion contains. In dark or cloudy days, when the sunlight is feeble and does not radiate violet rays, it is more probable that collodions rich in bromide will give better results than those which contain a large proportion of iodide. Bromo-iodized collodion for use in landscape-photography, according to experiment, ought to contain a much larger proportion of bromide than collodion for use in portraiture. It ought to contain twice as much bromide as iodide; at least, that is the rule for the wet process.

Silver chloride has not been employed, either in the wet process or in the dry process; at least, it has not been generally used.

In the dry process the presence of silver iodide with bromide is almost totally without effect, more particularly with alkaline development, which is now generally used. On the other hand, a small quantity of silver chloride added to the silver bromide is not hurtful for dry plates developed by a weak alkaline developer. The images are intense, but not always free from fog, and without doubt silver bromide ought to form the staple of dry plates.

The sensitiveness to light of the haloid salts of silver is not only influenced by the mode of preparation, but also by the mode of development. The alkaline development with pyrogalllic acid is much preferable to the acid development; but

the superiority of the new concentrated pyrogallic-acid developers, made strongly alkaline, over the old feebler developers that were formerly employed, is incontestable. This new mode of development was introduced by Wortley. When using very strong alkaline developers the smallest impact of light causes a reduction of silver bromide. Even the impact of the yellow and green rays, which are usually very feeble in their effect, are perfectly shown. Red light, however, affects the plate the least, and for this reason we are obliged to prepare very sensitive dry bromide plates (and particularly gelatino-bromide plates, of which we shall speak further on) in places lighted only with very deep ruby glass. Without this precaution the plates are spoilt. Tóth and myself found that a plate coated with a mixture of coralline and fuschine, dissolved in varnish, answered perfectly that object, and only allowed red rays to pass. Unfortunately these aniline colours bleach, and then allow blue rays to pass.

The manner in which light acts on the salts of silver is complicated, and becomes still more difficult when foreign substances are added to these salts. By adding certain substances to the haloid salts of silver, the action of light is diminished; whilst by adding others it is increased. The latter bodies are called sensitizers. H. W. Vogel has studied these sensitizers, in all their details and all the effects, from two points of view. The study of these bodies is not only of capital importance for theoretical photo-chemistry, but also opens out researches of the greatest interest in practical photography and modern chromo-photography.

CHAPTER V.

SENSITIZERS.

By adding colouring-matter to a (silver bromide) dry plate the sensitiveness of the silver bromide is augmented by the rays which the colouring-matter absorbs. In this manner the bromide is rendered sensitive to colours by which they are little if at all impressed. Such bodies which so act are called *optical sensitizers*. Certain combinations, however, have the property of aiding the decomposition of silver bromide by light. In this category are the bodies which combine with iodine and bromine, and which thus favour the decomposition of silver iodide into sub-iodide and iodine. Compounds of this kind are called chemical sensitizers. According to Poitevin and Vogel, the bodies which readily absorb iodine and bromine are good chemical sensitizers. Captain Abney is of the same opinion; but Carey Lea is of the opinion that the affinity of the body for iodine has less importance than has its affinity for oxygen, and that chemical sensitizers ought to be reducing bodies. (Poggendorf, "Bulletin," 1877, vol. i, p. 563.) H. W. Vogel has energetically combated this opinion of Carey Lea. It is easy to imagine a body which unites together the property of being a chemical sensitizer and also an optical sensitizer, and the division of these two classes of sensitizers has been combated at different times. The arguments, however, which have been brought forward against this kind of division do not appear to be sufficiently weighty for it to be abandoned; for it cannot be denied that there is a great deal to be said for it. Many substances destroy or diminish the sensitiveness of salts of silver to light. Nitric acid particularly impedes the development of iodide or bromide of silver when exposed to the light, even when the solution is but little concentrated (SG.=1.2). When the acid is more dilute it does not destroy the sensitiveness of the salts of silver; it only makes it less. Hydrochloric acid has the same effect. Sulphuric

acid and acetic acid in small quantities also diminish sensitive-ness. Dilute acid and acid vapours, more particularly nitrous acid, destroy, little by little, the latent image on a washed film of iodide of silver in collodion. Silver chloride darkens in the light, even when exposed to concentrated nitric acid; but, on the other hand, it does not blacken when it contains even a trace of mercuric chloride. Hydriodic acid prevents the darkening by light of silver iodide (Rodwell, "Proc. Roy. Soc.," 1877).

Silver iodide containing an excess of potassium iodide is almost entirely insensitive to light. Even when the excess of potassium iodide has been almost completely eliminated by washing, the insensitiveness is still present, although by prolonging the exposure for a very long time an image is obtained by using an iron-developer with silver nitrate (Carey Lea, Vogel, "Phot. Corr.," vol. viii, p. 181). The anti-photographic properties of potassium iodide are also to be remarked by applying it to the latent image. The impression made by light disappears. It must, however, be remembered that potassium iodide does not act in the same manner on all latent images. Silver iodide impressed in the presence of silver nitrate, and treated with potassium iodide, loses all trace of an impression, whilst with bromo-iodide of silver the image is only enfeebled; the image on silver iodide produced in the presence of organic matter is not destroyed by potassium iodide (Vogel, "Phot. Corr.," vol. viii, p. 243). By treating plates prepared with silver bromide emulsion with a dilute solution of nitric acid and potassium bromide all luminous impression is effaced, and the plate can be re-used. Chlorine, bromine, or cupric chloride can also be substituted. Silver iodide precipitated in an excess of silver nitrate and washed is, according to Schultz-Sellack, from ten to twenty times more sensitive than that prepared with an excess of potassium iodide, although the two can be considered as pure.

Potassium iodide acts in a singular manner upon silver-chloride paper: it destroys even the direct impression. If a chloride of silver paper blackened in the light be brushed over with a solution of potassium iodide, and be then exposed to the light, it soon bleaches, afterwards becoming quite yellow; it then darkens when the luminous action is con-

tinued. (It appears that in darkness it disengages hydrogen.) The paper bleaches more rapidly in the violet rays than in the red or green rays (Hunt, "Researches on Light"). Potassium iodide destroys the latent image equally as well as the direct image.

Similarly an excess of potassium bromide also reduces the luminous impression quite as well when it acts upon silver bromide as on the iodide, even when the bromide has been carefully eliminated by washing. Silver bromide and iodide produced in this manner are less sensitive than those precipitated by an excess of silver nitrate and then washed (according to Vogel, four times) in pure water. The difference is not, however, so visible as in silver iodide in presence of potassium iodide. In the emulsion process, in which the bromide is precipitated in an excess of potassium bromide, it is important to know the effects produced. In general, emulsions precipitated in excess of silver nitrate are more sensitive than the others, although the sensitiveness of those precipitated in an excess of bromide can be increased by using an organic sensitizer, such as tannin, resin, or gum.

An excess of chloride does not act so anti-photographically as the iodide and bromide of potassium. Bromide of silver emulsions, in which the excess of silver nitrate has been precipitated by an excess of chloride and afterwards washed, are only slightly less sensitive with alkaline development than emulsions containing an excess of nitrate which is subsequently removed by washing.

It is interesting to remark, that it is possible to determine, by the colour of a negative developed by the alkaline method, whether the silver bromide has been prepared with an excess of nitrate or bromide. In the first case, the negative has a greenish colour; in the second, a ruddy or brown tint (Wortley, "Photographic News," vol. xv, p. 291).*

The sensitiveness to coloured rays, as it is with white light is diminished by the addition of potassium bromide to the emulsion. The spectrum appears altogether more feeble;

[* This is hardly exact. The green or brown colour can be given to a collodion-emulsion negative, according to the length of exposure (see "Photo. News," vol. xv, pp. 322 and 479).—*Editor.*]

but the yellow region more particularly resents this addition. Moreover, if dry silver bromide is treated with a slight excess of soluble chloride, a decrease in sensitiveness for white light, as well as for the coloured rays, is to be remarked, but this diminution is much less strongly marked than in the preceding case.

I conclude, from this, that it is best either to prepare emulsions with an excess of silver nitrate (though they are, it is true, more sensitive, yet they spoil by keeping, and more easily give fog than others), or to use a soluble chloride in excess, when it is desired to have the most stable emulsions and, at the same time, the most sensitive; a soluble bromide in excess diminishes the sensitiveness in the highest degree.

The advice which certain photographers give, to add a little nitric acid, or nitro-muriatic acid, to the emulsion to prevent fog, ought not to be followed, except with great caution; for emulsions of this kind easily lose every trace of the latent image, if too long a time elapses between exposure and development.

Amongst sensitizers, silver nitrate especially acts with great energy. A concentrated solution of silver nitrate (10 per cent.) increases the sensitiveness of the chloride, the bromide, and more particularly the iodide of silver. The latent action of light on silver iodide is enormously increased by the addition of silver nitrate. It is less strongly shown on silver bromide; but with silver chloride the direct action of light is much increased. In the wet-negative process this method is adopted when the bromo-iodide of silver is exposed in the presence of silver nitrate. By washing off the nitrate the sensitiveness of the plate is greatly diminished, although even small quantities of nitrate enormously increase the action that light exercises on the plate.

Vogel explains this phenomenon by the great affinity that silver nitrate has for bromine and iodine, which greatly aids the splitting up of the molecule of haloid silver by light. Silver nitrate is a greater sensitizer than all the organic sensitizers. Modern alkaline development allows the preparation of instantaneous plates without excess of silver nitrate. Silver nitrate, although colourless, exercises an influence on the sensitiveness to colours, as I have already remarked above;

it augments more particularly the sensitiveness to the most refrangible rays (blue-violet). The following bodies act as sensitizers :—

Mercurous nitrate, stannous chloride, sodium sulphite, sodium nitrite, soda, caustic potash, sodium-arsenite, tannin, pyrogallie acid, potassium, ferrocyanide, which not only accelerate the blackening by light when they are in direct contact with silver iodide, but also increase the darkening in development. Dry plates made with silver iodide, when coated with these substances, give stronger and more vigorous negatives. As Vogel has shown ("Pogg. Ann.," vol. 195, p. 518), all these bodies have a great affinity for iodine.

A body which especially increases the sensitiveness of silver bromide is gelatine, which Poitevin (Martin, "Manuel de Photographie," 1857, p. 145) had already used to replace collodion in the production of films of silver iodide, and which Norris later, in 1856, brought forward as a preservative for washed silver iodide plates. Norris used a mixture of gelatine and gum, to which he added a minute quantity of glycerine ("Photographic Journal," 1856, p. 257).*

These facts are all the more interesting, as at the present time gelatine emulsions (bromide held in suspension in gelatine) are so much in vogue, as were collodion emulsions sensitized by gelatine. Wilde has proposed to precipitate collodio-bromide emulsions by means of an aqueous solution of gelatine. Obernetter coats his collodio-bromide emulsions with an alcoholized solution of gelatine and water ("Phot. Mittheilungen," vol. xv, p. 266), which is Hill Norris's old plan. The sensitiveness of these collodio-gelatino-bromide plates greatly surpasses in rapidity the old iodide of silver plates.

The sensitiveness of gelatino-bromide plates is such that, in using alkaline development, portraits can be taken with much shorter exposure than that necessary for the production of images by wet collodion. On account of their extreme

* It is curious to see the notice made in 1840 by Hunt, who said that gum arrests the decoloration in iodide of silver chloride blackened by light. Gum arabic and gum tragacanth make the image much less stable.

sensitiveness even for the red rays, the infra-red region can easily be photographed.*

Even photographs have been taken of the Geissler-tube spectra, which could be taken by no other plates (Monckhoven; Poggendorf, "Beiblätter," vol. i, p. 286). Again, photographs of Cazin's sparks (Pogg., "Beibl.," vol. i, p. 287) have been recently made by Vogel with success ("Phot. Mitt.," vol. xv, p. 279). He discovered in the spectrum of oxygen, after an exposure of two hours, a new series of rays in the blue, the violet, and the ultra-violet. In the spectrum of hydrogen he also discovered a quantity of unknown rays, and could distinctly see the rays in the red. Gelatine emulsion is singularly sensitive to the red,† which must not be lost sight of in preparing it. In practice its sensitiveness for the yellow and green are also proportionately increased, and thus more perfect images can be obtained, in the sense that the lights and shades are more in relation to those which are to be found on the object itself.

Collodio-bromide emulsion covered with gelatine is not so sensitive as gelatino-bromide, although the sensitizing film of gelatine accelerates the action of the luminous rays. The great sensitiveness of gelatino-bromide of silver appears, then, to be due not to a particularly intense sensitiveness produced by the gelatine, but rather by a physical modification in the nature of the silver bromide. The experiments of Bennett and Monckhoven bear on this point.

Tannin is often employed as a preservative to collodion dry plates prepared with silver bromide or iodide. The tannin dry-plate process discovered by Russell has everywhere been a success, and is still employed with some few modifications. Tannin has also been employed as a preservative for emulsions; it increases the sensitiveness of plates for the violet, but above all for the green and yellow. Silver bromide plates,

[* There is a mistake here. The ultra-red rays cannot be photographed by ordinary gelatine plates: the gelatine itself in a measure prevents this being done.—*Editor.*]

[† The sensitiveness of gelatine plates to the red is not $\frac{1}{100}$ th of the same plates to the violet, and perhaps to the green they have $\frac{1}{10}$ th of the sensitiveness they have to the violet; hence the statement must be taken *cum grano salis*.—*Editor.*]

with an excess of silver nitrate, do not give greater sensitiveness by the introduction of tannin; but, in the presence of a slight excess of bromide, the influence of this body upon the silver bromide gives a very considerable increase of sensitiveness.

Morphia has no action on silver bromide when it is in the presence of an excess of nitrate: it even appears that it slows the action of light. On the other hand, it acts as an energetic sensitizer upon silver bromide formed with a slight excess of bromide. Silver bromo-iodide in a dry state, to which a little silver nitrate is added, is made more sensitive, not only to the blue and violet, but also to the green rays (H. W. Vogel).

Pyrogallic acid behaves in an analogous manner. (*See further on.*)

Salicine increases the sensitiveness of dry silver bromide for the red and yellow (Carey Lea, "Photographic News," 1874). It has been employed as a preservative for dry plates.

A small addition of resin to the collodion sensitizes washed-and-dried iodide and bromide of silver, all excess of silver nitrate being thus eliminated. For this reason, resins were employed, twenty years ago, as preservatives in dry plates. Abney has recently remarked that the addition of resin increases the sensitiveness of silver iodide and bromide to the red rays ("Monthly Notices of the Royal Astr. Soc.," 1875).

H. W. Vogel and Lohse ("Pogg. Ann.," vol. cxix, p. 297) have obtained upon plates of this description a reproduction of the spectrum as far as the extreme red,—according to Vogel, even to the ultra-red. For this reason resin has been recommended for dry plates, in order to photograph the yellow and red. Abney finds that these plates are ten times more sensitive to the blue than to the red and yellow regions ("Phot. News," 1876). Nevertheless, as H. W. Vogel has shown, the increase in sensitiveness to the red rays obtained by these plates is only a minimum. Abney himself has abandoned these resin plates, and now prefers another preparation of bromide sensitive to the red rays. (*See further on.*)

It follows from this that all rays have a chemical action on silver salts; and that, from the red to the extreme violet of the spectrum, all the rays act in a reducing manner.

The action of each particular ray depends not only on the nature of the salt of silver, but it also has an intimate connection with the sensitizer. The sensitizer acts especially upon the latent image,—that is to say, upon that which ought to appear by action of reducing agents; for, in speaking of sensitizers, we have always had in view the latent* action of light.

The manner in which the substances exposed to light behave optically towards coloured light is of the greatest influence. *It is only those rays which are stopped or absorbed by the substance sensitive to light which act chemically on it.* This law is important for the explanation of the chemical action of coloured rays.

Draper showed, in 1841, that all the coloured rays which act chemically on a substance are absorbed by them (Draper's Memoirs, "Phil. Mag.," vol. ix, p. 195; vol. li, p. 161).

Later, Schultz-Sellack produced silver iodide, bromide, and chloride in transparent slabs, and showed that the haloid salts of silver are chemically changed with a certain energy by all the rays they absorb. This difference of colour can be seen in the precipitates, which indicates different degrees of sensitiveness to light; thus pure silver iodide and bromide are feebly yellow. The precipitate of a mixture of these bodies with metallic bromo-iodides and chloro-iodides is an intense yellow.

H. W. Vogel has made the most conscientious studies upon the alteration of silver bromide by light. With nearly every sensitizer the optical absorbing action comes into play. A solution of silver nitrate sensitizes vigorously, only because the wet films of silver iodide and bromide absorb the blue rays better than dry plates of the same substances. Pyrogallie acid, on the other hand, acts better in a dry state, because when in solution it allows the chemical rays to pass. It is, therefore, necessary here to have a further action, that the chemical action should combine with the optical ("Phot. Mitt.," vol. viii, p. 133; "Pogg. Ann.," vol. cliii, p. 288).

[* We demur to the term, "the latent action of light." The effect of the action of light is visible or invisible: invisible with a short exposure; visible usually when the action is prolonged. It is a mere case of quantity of particles acted upon.—*Editor.*]

34. THE CHEMICAL EFFECT OF THE SPECTRUM.

If all the rays which are absorbed by a body are eliminated from the spectrum, the remaining rays are not capable of affecting a body. Thus, for instance, a luminous ray which traverses a solution of the double citrate of iron and ammonium has no more action on that salt; a luminous ray which passes through a mixture of hydrogen and chlorine does not act on a second mixture (Draper); a ray which passes through a solution of bichromate of potash will not decompose a mixture of this salt when in contact with organic matter; in the same way, chrysoidin is not bleached by a ray which has first passed through a sheet of gelatine coloured with chrysoidin.

CHAPTER VI.

DYED FILMS.

THE integration of the luminous rays acts upon many substances, and particularly upon silver compounds; but the rays which are the most actively absorbed are those which act in the most energetic manner. The decomposing action of the solar spectrum upon these compounds, *e.g.*, silver bromide, can be notably increased by the addition of colouring matters to this salt. The sensitiveness of the silver bromide is thus augmented, and especially for those rays which are absorbed by the matter which is added to it. (It is not necessary that the colouring matter should undergo any chemical* change.) Thanks to this method, it is possible to greatly augment the sensitiveness of the salts of silver to the red, yellow, or green rays.

In order to increase the sensitiveness of silver bromide to certain colours, an addition is made of colouring matter which absorbs precisely the rays of the spectrum to which it is desired to render the plate sensitive. The colouring matter can be added by dissolving it in collodio-bromide emulsion, or by flowing a solution of the colouring matter over a plate prepared with uncoloured emulsion. It is well to remark, that the maximum photographic activity does not coincide exactly with the locality of absorption, but is found slightly shifted towards the red extremity of the spectrum. There is nothing extraordinary in this, if the absorbing regions remain perfectly constant. This want of coincidence is explained by

[* We differ from the author here. It appears to us, any colouring matter, which is effective in the manner indicated above, is affected by light.—*Editor.*]

the law of Kundt.* In effect the zone of absorption recedes towards the red when the refractive index of the medium increases. In the preceding experiment the colouring matter, with the bromide suspended in the collodion, is enclosed in a more strongly refracting substance, and causes the accelerating action to shift towards the red (H. W. Vogel).

Colouring matter which is to be used to sensitize salts of silver, making allowance for solubility, should fulfil the following conditions :—

- 1st. It ought optically to absorb the light for which its collodion is to be sensitized.
- 2nd. It ought to absorb free iodine or bromine. In the contrary case, it is necessary to add a chemical sensitizer.
- 3rd. It should not decompose silver nitrate, for without this qualification it would hinder the preparation of the plate. (It is evident that for collodio-bromide of silver emulsions which do not contain pure silver nitrate this condition is unnecessary.)

Optical sensitizers require the presence of a chemical sensitizer. Certain colouring matters only show their sensitizing properties when they are in the presence of chemical sensitizers, *e.g.*, a small quantity of silver nitrate, of tannin, of morphia, &c. ; in presence of an excess of bromide or chloride, on the other hand, they are completely inert (H. W. Vogel, "Photo. Mitt.," vol. xiii, p. 31). Regions of sharply increased intensity in plates of silver bromide, coloured by different matters, are only found when the corresponding colour of the spectrum in the absorbing regions is very strongly shown. Colours which do not possess the power of absorbing certain rays of the spectrum will never be seen, according to Waterhouse (it would be more correct to say, will never be *distinctly* seen), to give an increase of intensity, even when these substances markedly lend themselves as sensitizers of silver-bromide dry plates. Fluorescent colours seem

[* A law not established like that of gravitation. Kundt's experiments may be explained on other grounds.—*Editor.*]

also to be particularly apt to produce this effect. All colouring matter does not augment the sensitiveness of the different salts of silver in the same manner; thus fuchsin, for example, renders silver bromide very sensitive to the yellow rays, whilst it only influences the chloride very slightly.

Coralline and aurine in solution absorb the yellow and green rays of the spectrum. If silver bromide is coloured by means of these two substances, it becomes as sensitive to the indigo as to the yellow—a colour to which, by itself, it is but little sensitive. In the blue region the action shows itself less strongly, for the silver bromide is already in itself sensitive to yellow and blue rays. The addition of a colouring matter augments the sensitiveness, in the place where coralline shows an absorption band. There is, however, a great difference between the different kinds of coralline found in commerce. They act also in quite a different manner. According to Carey Lea, by the addition of coralline the sensitiveness of silver bromide is greatly increased, more especially for the red rays; the action of the yellow rays is slightly intensified; while that of the green rays is unchanged. The same substance diminishes the sensitiveness of silver iodide in the red (*"Jahresbericht Chem.,"* 1875, p. 147). The experiments of H. W. Vogel in regard to the action of coralline upon silver iodide do not give the same results. Vogel has found that the action of coralline on silver iodide is the same as on the bromide.*

* According to the experiments of Carey Lea (*Silliman, "Amer. Journ."* (3), vol. vii, p. 200), the following substances are subject to very varied changes when they are exposed to coloured light, and in presence of colouring matters indicated further on. These substances are—ammoniacal oxide of iron, potassium bichromate, potassium ferrocyanide, uranic nitrate, silver chloride, bromide and iodide of the same metal. The colouring matters are aurin, aniline blue, and green, tincture of saffron, coralline, aniline red, and mauvine. It is to be remarked that Carey Lea operated with coloured glasses, and not with the solar spectrum. Quite recently, Gros (*"Compt. Rend.,"* vol. clxxxviii, p. 79) has treated of the action of differently coloured rays on a film of silver bromide impregnated with different colouring matters. Becquerel remarks, to complete the research, that collodio-bromide of silver plates with an excess of potassium bromide become more sensitive to the rays absorbed by the following substances:—Alcoholic chlorophyl, carthainine curcuma, extract of red currants, and mauve, and finally hæmaglobin. I have received his work too late to be able to take it into consideration.

Coralline acts most markedly in the yellow region on silver chloride plates near D, and as far as G and C. They are thus more generally sensitive to light than pure silver chloride. They render yellow the best; red and green less well; whilst blue is very badly rendered. A mixture of bromide and chloride of silver in collodion gives, when their relative sensitiveness to colours is taken into account, a mean between the two. Such plates are very sensitive to the yellow near D; the second maximum of sensitiveness is found at B; between the violet and yellow regions they only show a very feeble action.*

Silver bromo-iodide containing a certain quantity of coralline has its maximum of sensitiveness at G. The sensitiveness then falls rapidly, to ascend again at F. This substance shows a greater sensitiveness for deep blue than for light blue. Exposed in the wet state, with free silver nitrate, the maximum intensity is at F, and afterwards at G. The blue produces the strongest action; the violet a less action (H. W. Vogel and Becquerel)

Ducros du Hauron found that aurine (orange coralline) also increases the sensitiveness of silver bromide for the green rays. But it was necessary that the bromide should be produced in the presence of an excess of silver nitrate. He wished to utilize the quality to produce negatives for use in his chromo-photography.

All the above statements refer to the latent action (*see* Note, p. 33) of light, which is only made visible by the action of reducing agents.

Naphthaline red increases the sensitiveness of silver bromide for the yellow region (from near D to C), as also for the violet region. It is only necessary that the bromide be produced in the presence of a slight excess of silver nitrate.

A great quantity of colouring matter—this applies generally—does not increase the sensitiveness for that part of the spectrum, but, on the contrary, rather diminishes it. With a redder coloration of the film of silver bromide all sensitiveness to the yellow is destroyed. H. W. Vogel explains this apparent paradox in the following manner:—A strong film

* To study absorption spectra of different colouring matters, see H. W. Vogel's "Analyse Spectrale Pratique." Nordlingen, 1877.

of colour absorbs the light before it can reach the silver bromide, and the luminous rays cannot make the coloured molecule of silver bromide vibrate rapidly enough. It is altogether otherwise when the density of the colouring matter is diminished. Thus the luminous rays, after having traversed the top film, have still force enough to put the neighbouring molecules energetically into vibration ("Berliner Berichte," Bd. vii, p. 976; "Chem. Centralb.," 1874, p. 561). If the silver bromide contains an excess of potassium bromide, no increase of sensitiveness for any particular colour is to be remarked; it is only when a little silver nitrate, tannin, morphia, or other chemical sensitizer is added that the sensitiveness to the yellow is increased.*

Fuchsine (aniline red) does not give sensitiveness to silver bromide to any colour of the spectrum. It renders silver bromide, when it contains a trace of free silver nitrate, completely insensitive. At the same time, the sensitiveness to the blue is diminished, probably because aniline red makes the silver bromide more translucent to the blue rays, and, consequently, only slightly augments its sensitiveness.

According to Waterhouse, naphthaline red increases the sensitiveness for the yellow, but diminishes it for the green

[* The above is Dr. Vogel's explanation of the matter, and of the reason of coloured films acting when the colouring matter is small in quantity, and not acting when the colouring matter is large in quantity. I must enter a protest at once against all theories of the existence of optical sensitizers: it is against all known laws of molecular physics. If the theory of optical sensitizers were correct, we should have to believe that a ray of some particular refrangibility, which was absorbed by a dye, was, in its partially absorbed state, capable of acting more vigorously on the salt of silver than the same ray totally unabsorbed could do. If a ray which is absorbed is capable of setting up phosphorescence, then the change in refrangibility of the ray might account for it; but this seems improbable, since in that case the refrangibility of the impinging ray would have to be greater than the phosphorescent ray, which is contrary to Stokes's law. A combination between the dye and free silver nitrate, when the emulsion is prepared with an excess of silver, or the action of light on the dye itself (thus forming an oxidized nucleus for the depositing silver during development), will account for the phenomenon without doing violence to known physical laws. Later experiments have shown that, without any chemical sensitizer being present, when the emulsion has been prepared with excess of bromide the same action occurs, which eliminates the only objection to the simple explanation offered, as opposed to Vogel's.—*Editor.*]

and the red. Violet and purple colours augment the sensitiveness for the yellow and orange, but diminish that of the green.

The addition of fuchsine to silver chloride only produces a feeble increase of sensitiveness for the yellow. On the other hand, sensitiveness for the violet is exceptionally increased; it is greater than with pure silver chloride. In the presence of free silver nitrate and of fuchsine the sensitiveness for the indigo and blue rays is much increased (H. W. Vogel, "Phot. Corr.," vol. ii, p. 202).

Aldehyde green and picrate of methyl-rosaniline greatly increase the sensitiveness of silver bromide for the yellow-orange (between C and D), and, at the same time, for the blue. Aldehyde green is, at the same time, an optical and chemical sensitizer; in fact, it absorbs iodine and bromine, and gives sensitiveness for the yellow-orange rays. It is not necessary, therefore, with silver bromide, to use with it a chemical sensitizer, as it is one in itself. It has almost the same action on silver iodide as on silver bromide (H. W. Vogel; Becquerel, "Phot. Mitt.," 1874, p. 139).

Eosin in solution shows a band from E to F. Added to the silver bromide emulsion, it sensitizes it for the green rays. Films of this nature are infinitely more sensitive to the green and yellow than to the blue and violet of the spectrum.* The maximum of action is found from G to F. From the blue to the violet the action is very feeble. Wet plates prepared with silver bromo-iodide and an excess of silver nitrate, and coloured with eosin, are sensitive to the green and yellow, although their maximum sensitiveness is situated at the violet extremity of the spectrum. Small quantities of acid retard the sensitizing action (H. W. Vogel, "Phot. Mitt.," vol. xiv, p. 19; Waterhouse, "Pogg. Ann.," vol. clix, p. 616). When Waterhouse tried collodion stained with eosin for dry plates, and for wet plates prepared with silver bromide and iodide on landscapes, bouquets of flowers, &c., he did not observe any very favourable results. He had, it is true, a slight increase of sensitiveness for the yellow rays; but he did not observe any intensification in the green of trees. The exposure given

[* The blue and violet are still far the most active, according to our experience.—*Editor.*]

was three times that which would have been required for wet collodion, and this although the collodion was only slightly coloured.

Chlorophyl strongly sensitizes silver bromide and iodide chiefly in the red, about the regions where the rays are absorbed. In the red and yellow regions of the spectrum we see several maxima of intensity, which correspond to the absorption-bands of chlorophyl, the one between B and C, and the other between C and E. With a short exposure, the films are sensitive to E in the green, and it is only after a more prolonged exposure that the action in the red is seen. The sensitiveness in the red is five to ten times less than in the violet (Becquerel, "Compt. Rend.," vol. lxxix, p. 189).

The colouring matter of turmeric increases the sensitiveness of silver bromide to the less refrangible rays. If to collodio-bromide of silver an alcoholic solution of turmeric (seeds) is added, till a brilliant yellow colour is obtained, this collodion becomes more sensitive to the yellow and red than if it is sensitized with anything else. The plates show a diminution of intensity from G to F; after that an increase of intensity from B in the green as far as D in the yellow, from which point it gradually diminishes to A (Waterhouse).

Methyl violet makes silver bromide very sensitive to the yellow, near D.

Cyanin blue, itself sensitive to the light, renders silver bromide sensitive to the colours which itself absorbs; it sensitizes for the yellow and orange, and this in such a manner that a plate is more sensitive to these colours than to the violet.* The maximum effect is at D and C (Waterhouse).

If silver bromide contains only a trace of soluble bromide, Vogel finds that it does not become sensitive to the yellow; cyanin blue only is decomposed by yellow light. If normal collodion stained with cyanin is flowed over a plate, and exposed to the solar spectrum, and it is afterwards covered with silver bromide emulsion and developed without further exposure, a deposit is found in the part of the plates where the yellow light has acted,† in the same place where the

[* See previous Note.—*Editor.*]

† "Photographic Journal."

absorption bands of cyanin are found. By adding colouring matter to the emulsion, and afterwards exposing, the same results are obtained. Abney concludes from this that the reduction of colouring matter precedes the decomposition of the silver bromide, and that the good effect obtained by the addition of colouring matter should be always referred to a purely chemical action; and that the more readily the colouring matter combines with the salt of silver, the more readily would it be acted upon (*see* above). He does not, therefore, agree to Vogel's theory as to the chemical sensitizers and optical sensitizers.

H. W. Vogel has successfully refuted Abney's opinion ("Phot. Mitt.," vol. xv, p. 91). He considers that sometimes a combination between the colouring matter and the silver nitrate takes place when the latter is in excess (*e.g.*, with aniline red); and yet, when the excess of silver nitrate does not exist, the aniline red acts also very strongly as a sensitizer for the yellow rays when a chemical sensitizer, such as tannin or morphia, is added.* It cannot then be a question here of a combination sensitive to light formed with the morphia and colouring matter. There are optical sensitizers which at the same time absorb bromine, which are also chemical sensitizers (*e.g.*, aldehyde green). Abney's supposition, which he bases on an experiment with cyanin blue, which appears to prove that the colouring matter undergoes first of all an alteration and a reduction, and that it is this reduction which is the cause of the chromatic sensitiveness, is not admitted by Vogel, who says that on this hypothesis chemical sensitizers—whose presence, besides the colouring matter, is necessary—would be superfluous. Abney's proposition (who says that colouring matter in presence of silver bromide is more sensitive than when it is alone) is opposed to the hypothesis of a primary reduction of the colouring matter and its subsequent action on the silver bromide.†

* See note to page 39.

[† We say, "not proven." The dye on a film may be only $\frac{1}{100000}$ of a grain, and that distributed round each particle of the silver salt, thus exposing an enormous surface on which light can act. The minutest alteration in the dye would cause a nucleus sufficient for developing purposes, exactly in the same way that the minute portion of subsalt of silver forms a nucleus.—*Editor.*]

Abney's remarks, then, only apply to special cases of colouring matter of strong sensitiveness to the light. This rare case was present only with very long exposures; but it is not possible to apply it when latent images are obtained on coloured silver bromide and with a short exposure. I say short exposure, for we have, in the foregoing experiments, spoken of exposures of short duration.

Many other colouring matters do not increase the sensitiveness, according to Vogel, of the silver salts for the spectrum colours, although they themselves absorb certain luminous rays. Thus, for instance, picric acid, aniline blue, ultra-marine, lake, indigo, and purpurin do not increase the sensitiveness of silver bromide coloured with them.

Aniline blue, however, produces irregularity of action in its behaviour with silver bromide. It does not increase the sensitiveness of that salt for the colours it absorbs. According to Waterhouse, it increases the sensitiveness of the bromide for the blue rays, but very little for the green or orange rays.

Although it is possible to make photographic plates sensitive to all the colours of the spectrum, from the red to the violet, by adding colouring matter to them, it is not possible, however, to reproduce the yellow in nature with the same facility and the same exposure as the violet. In pictures, natural flowers, &c., the yellow and red develop, in spite of the bromide sensitized for the yellow and red, much worse than the blue and violet.

The reason of this is, that the relative brightness of yellow, on the one hand, and of the blue on the other, is not so sensibly different, since the feeble chemical action of the yellow and red arrests the action of the blue (the yellow is often optically lighter than the blue). On the other hand, the yellow of the spectrum is one hundred times brighter than the blue of the spectrum, and acts also in these very favourable circumstances as energetically as the blue. In nature the difference of brightness is less sensible.*

[* We cannot agree with the author in this. The yellow of nature is reflected light. It might be said that light from the sky exhibits the same deficiency of yellow as sun-light. This is not the case, however. No dried film, in our experience, is nearly so sensitive to the yellow as to the blue of the spectrum.—*Editor.*]

If it is desired, to reproduce natural objects, so as to have a proper rendering of blue and yellow, the blue must be toned down by yellow glasses.

It was upon such considerations that the discovery of photography in natural colours by indirect means was thought of and put in practice at the same time by Cros and Ducos du Hauron in 1869, and another anonymous person. Whilst Cros was contented to make known the theory of the process, Ducos du Hauron had tried to carry it out practically.

After long researches, Ducos du Hauron produced coloured photographs in the following manner (*see* "Photo. News," vol. xx, and "Traité Pratique de Photographie des Couleurs," 1878, Ducos du Hauron):—He produces in the camera three different images, that is to say, one by green, another by orange, and another by violet light, and the model is photographed through glasses thus coloured. From these negatives three coloured positives are made, in red, green, and blue, called monochromes, and these three positives are superposed, and by the mixture of tints an image in natural colours is obtained.

The red monochrome is obtained from the negative produced with green light; the blue monochrome from the negative given by orange light; and the yellow from a negative taken with violet light. Why are there three different negatives? and why also this diversity—this *chassé croisé* of colours? We give the words of the inventor:—

"Chacun de ces trois monochromes étant constitué par une préparation douée de transparence, et susceptible d'être fixée par la lumière, et, proportionnellement à cette action, chacun d'eux, par l'effet de l'interversion de couleurs qui vient d'être spécifiée, donnera nécessairement, soit comme gradation des clairs et des ombres, soit comme répartition de la couleur spéciale des objets, l'image voulue.

"Et d'abord, comme gradation des clairs et des ombres, abstraction faite de la couleur spéciale des objets à représenter, chacun des trois monochromes sera évidemment exact. Chacun d'eux, en effet, étant fourni par un cliché négatif qui traduit les noirs du modèle par du blanc et les blancs du modèle par du noir, traduira à son tour les noirs du modèle par la préparation rouge, bleue ou jaune propre à ce monochrome; et ce rouge,

ou ce bleu, ou ce jaune sera d'autant plus intense, que le noir du modèle sera plus noir ; et réciproquement, chacun d'eux traduira les blancs du modèle par l'absence de matière colorante, cette matière colorante étant éliminée sous les noirs du négatif, et d'autant plus éliminée que le blanc du modèle sera plus blanc.

“En second lieu, comme répartition de la couleur spéciale aux objets qu'il s'agit de représenter, chacun des trois monochromes sera non moins exact, et c'est cette répartition qui engendrera, d'un monochrome à l'autre, les différences qu'ils doivent offrir, et qui ne naîtraient pas de la simple traduction des clairs et des ombres. Prenons pour exemple le monochrome *rouge*, fourni par le négatif qui est dû à la lumière *verte*. Comme le verre ou milieu transparent de couleur verte qui filtre cette lumière laisse passer presque exclusivement les rayons verts, et qu'il intercepte d'autant plus d'autres rayons que leur totalité se rapproche davantage du rouge, et comme, d'autre part, les objets de la nature qui émettent abondamment les rayons verts sont les objets jaunes, les verts et les bleus, il en résulte que le négatif en question traduira par du noir les surfaces jaunes, les vertes et les bleues ; que la préparation rouge du monochrome fourni par ce négatif traduira les rouges du modèle par du rouge, et par un rouge d'autant plus intense que le rouge du modèle sera plus prononcé ; qu'enfin cette même préparation rouge sera éliminée sous les noirs du négatif, c'est-à-dire dans les parties du susdit monochrome qui correspondent aux surfaces jaunes, aux vertes et aux bleues, et que cette élimination sera d'autant plus forte que ce jaune, ce vert et ce bleu seront plus prononcés. Un raisonnement analogue s'applique à chacun des deux autres monochromes ; contiendront l'un et l'autre une fidèle répartition de la couleur spéciale, soit simple, soit mélangée, qu'ils sont tenus de représenter.”

These three monochromes, placed the one upon the other, and coinciding in all parts, produce upon a white background a mixture of colours,—that is to say, a polychromatic image.

Plates of coloured glass are placed before the lens or before the sensitive plate. They are prepared by covering white glass with varnish, coloured in the usual manner. The plates must have the necessary depth of colour.

The three negatives of the different coloured images are obtained upon collodio-bromide of silver containing eosine, either dry (sensitized with tannin) or wet (with excess of silver nitrate). The development is done with an alkaline solution of pyrogalllic acid. This collodion gives with an equal fidelity the image after passing through violet, orange, or green glass. The same preparation is thus used for the three colours.

The negatives are printed on coloured carbon tissue (bichromate process). For red, carmine; for blue, prussian blue; and yellow, saffron-colour. These prints are carefully superposed one on another, so as to give a faithful representation of the natural colour.

Through the possibility of obtaining images of objects coloured by means of negatives obtained through different coloured glasses, Husnik brought out a new process in 1870 ("Photo. News," 1870): he proposed to print over each other coloured Lichtdrucks produced by the three negatives.

Albert of Munich has, after numerous and long trials, realised the idea, and produced by phototype coloured photographic images. He thus obtained the same effects as Ducos du Hauron, though more rapidly, and made it possible to obtain more proofs in a given time; besides which the exact superposition of the three impressions is more easily carried out. The production of negatives through green and orange glasses, according to the experiments of Albert of Munich and Marion of Paris, presents great difficulties. Husnik believes that a short preliminary exposure of the silver bromide to violet light really increases the sensitiveness to the yellow and red (above all, with the chloride and fluoride of silver), and the united experiments of several years on the action of a short preliminary exposure give weight to his opinion.

I can certify that Albert's experiments have resulted in very beautiful photographs in natural colours. I have seen very successful phototypes in colour due to him at the Photographic Society of Vienna. (As to the difficulties which he encountered in his trials, *see* Zaffé, "Photo. Corr." 1878, p. 139.)

This manner of settling the question of photography in

colours, which is as old as photography itself, is extremely remarkable. It is true it does not respond to the first and fundamental idea that the coloured image should be directly produced in the camera by the exposure of a sensitive plate to light. Direct photography in natural colours, in which a coloured image is produced on a sensitive plate, will be, like some other things, a long time before being accomplished.

CHAPTER VII.

REVERSED ACTION OF LIGHT.

THE colours of the directly coloured prints thus obtained leave much to be desired ; and, notwithstanding the long years of toil of Nièpce, Poitevin, Zenker, and Flourens, the fixing of the image is not yet accomplished. (*See the monograph of Zenker on photography in natural colours.*) By this plan satisfactory results have not yet been obtained, and the future will scarcely furnish them. The last method described is better for obtaining large coloured photographs. And, after what has been written, it is scarcely easy to solve the question as to how the different rays of the spectrum act on the haloid salts of silver. The sensitiveness to the reducing action of light can extend from the infra-red to the ultra-violet. Sometimes the photo-chemical sensitizers strongly influence the manner in which this action takes place. But, on the other hand, we believe that light can also produce an oxidizing action on the same compounds of silver ; red light mostly favouring oxidation, and violet light reduction.

In many cases the red and the violet have the same action upon the bromide and iodide of silver : thus there is reduction from the ultra-violet to the infra-red, as has been said before. This is as applicable to Daguerreotype plates developed with mercury as to dry plates which are covered with such or such a preservative, and developed by the alkaline or acid methods. The course of the reduction is always identically the same, even if the sensitiveness of the film varies with the surroundings. The numerous researches before mentioned prove this. It can be concluded, then, that all the rays of the spectrum possess a reducing action on the salts of silver.

On the other hand, it has frequently been remarked that red light produces an action altogether contrary to that of

violet light. The action of white light on a Daguerreotype plate is found to be strongly impeded by rays which have traversed a red, orange, or yellow glass, and the plate only slightly retains the property of taking the mercury (Claudet, "Comp. Rend.," vol. xxv, p. 554). The action of violet light on Daguerreotype plates is found to be strongly neutralized by red light (Herschel, Lerebours, Draper, Fizeau, Foucault). In the collodion process, the salts of silver behave in exactly the same manner, whether with alkaline or acid development.

If an image of the spectrum is received on a slightly veiled gelatino-bromide plate (having a slight excess of silver), the red region destroys the metallic silver, while in the violet the reduction takes place rapidly. Consequently, in fogged plates the photographic spectrum, after development, is positive at the red end; in other words, where the red light has acted, there is no metallic silver: the Fraunhofer lines alone are in metallic silver, appearing as positive. This reversal of the action of light is not only found in the red, but also in the violet (Waterhouse, "Photo. News," 1875). A gelatino-bromide plate is exposed for an instant to daylight, and then an image of the spectrum is allowed to fall upon it; in development (alkaline) not only the portions lighted by the spectrum, which are most coloured, but also those which have been impressed by the darkest rays, and where, consequently, light has not acted, are reversed.

This reversal of the action of light extends, according to Waterhouse, from the infra-red to the violet, and is produced in any kind of light (perhaps, but the fact is not yet proved, it may be found due to oxidation).

Later, Abney has tried to prove that the red and infra-red rays favour oxidation, and that in collodio-bromide they have an action directly opposite to those of the violet rays. He explains the variable action of the spectrum on collodio-bromide by the presence in the silver iodide and bromide of two kinds of molecules, one of which absorbs the red, and the other the blue rays.

Abney ("Bulletin de l'Association Belge de Phot.," 1878, vol. v, p. 115) takes up the idea thrown out by Lockyer, in a note published in the "Proceedings of the Royal Society of London," 1874, treating of the molecular theory applied to spectroscopic researches. He said, in a few words, that it

can be admitted that all matter is constituted of two different kinds of molecular groupings,—one absorbs in the red region, and the other in the blue region, of the spectrum; and that a combination of these two kinds of molecules would explain all the other phenomena.

This was the point of departure in Abney's researches. It can be admitted in all security that, when there is no absorption of light, no work can be done by light, whilst, when there is an absorption, work of some kind must be done.

The ordinary state of silver bromide and iodide is yellow, and consequently the maximum of absorption is in the blue end of the spectrum, and is more sensitive for it. Abney found that it is possible so to modify the molecular form of silver bromide as to render it sensitive for the red and infra-red; because it absorbed those rays. At first he tried to augment the weights and the volume of the molecule by the addition of resin to the emulsion; but in this way he did not get any very satisfactory results. The increase of weight gave more the idea of the formation of a new compound of silver than the existence of a new molecular combination.

Later, Abney obtained silver bromide in a new form, which absorbed red light, transmitting consequently blue, whilst in ordinary silver bromide the reverse took place. The identity of the composition of the two forms of bromide was proved by the fact that friction transformed the first into the second. There was thus only a molecular difference between the two forms of bromide.

To obtain a collodio-bromide emulsion absorbing the red, a particular operation was carried out. A collodio-bromide emulsion* is evaporated by heat to the consistency of jelly. Such an emulsion will give a film sensitive to the red rays; at least it will, in all probability.†

Abney obtained spectrum photographs—the red and the violet appearing well, whilst the yellow was completely missing.

* It is to be remarked that, by a long digestion with heat, gelatine emulsions become, in general, more sensitive to light, and probably also in the same circumstances more sensitive to the red.

† A horny collodion allows fewer red rays to pass than does a powdery collodion. A cotton for collodion more or less powdery also gives better results for emulsions which ought to be sensitive to the red (Abney, "Bull. Assoc. Belg.," vol. v, p. 116).

Thus the presence of two kinds of molecules was found (and up to a certain point this is probably the case in all emulsions).

Abney also photographed a spectrum, cutting off the blue by a red glass. He also was able to photograph the infra-red.*

He also found that the red accelerated oxidation, and that from this fact was to be found an explanation of the phenomenon of solarization, and perhaps also of the photography in colours of Becquerel and Niépce de St. Victor. Abney showed, by the following experiment, that in reality the red and infra-red accelerate oxidation. He prepared a plate with an emulsion sensitive to the red, exposed it two or three seconds to diffused light, after which he plunged it in a bath containing an oxidizing substance (permanganate or bichromate of potash, nitric acid, or peroxide of hydrogen). The solutions were very weak, *e.g.*, five or six drops of nitric acid in an ounce of water.†

Thus immersed, the plate was submitted to the spectrum for seven minutes, and, on development, not only had the red rays stopped the reduction, but had cleared away the fog; whilst on a transparent background the Fraunhofer lines had been left opaque.

Silver iodide behaves in the same manner as the bromide. The film was washed and exposed in a solution, and then developed by pyrogallic acid. Even by itself, and without an oxidizing solution, a film of bromo-iodide of silver was oxidized by red light in the same way as indicated above. On a film, on which the red exercised no reducing action, the oxidizing action acted without the use of oxidizing solutions. We have thus in photography rays which have a strong tendency to oxidize; and if one has not at his disposal a salt more sensitive to reduction than to oxidation in the air and red light, a reversed image on that part of the spectrum cannot

* By the aid of a Rutherford diffraction grating. In this way the wavelengths of the ultra-red could be determined.

† Abney thinks that with weaker solutions the oxidation and reduction mutually destroy each other. [Not quite so. He thinks that with weaker solutions the reducing action overpowers the oxidizing action, and with stronger solutions the image is destroyed without the helping action of red light.—*Editor.*]

be obtained. Ordinary wet plates of silver bromide are insensitive to the red, on account of the nitric acid necessarily present with them for the avoidance of fog.

If the red rays are favourable for oxidation, it is not said that on that account this property is completely absent in the blue rays. With these latter it is the deoxidizing action, on the whole, which predominates. When all the silver is reduced by the action of light, then the oxidizing action commences; the image disappears, and the phenomenon of solarization shows itself. The following experiment proves that the action is an oxidizing one:—A plate of silver bromide is exposed till it darkens; after which it is treated for some minutes with drops of peroxide of hydrogen, permanganate or bichromate of potash, and a difference in colour is scarcely perceived.

Sodium hyposulphite fixes those parts alone with clearness and without veil—the parts treated with the oxidizing substances; whilst the rest is covered with a slight veil of silver. It can be concluded from these experiments that each part of the spectrum exercises an oxidizing action upon a silver compound in a feeble degree of concentration.

Abney undertook a new series of experiments as to the way in which silver iodide behaved. To effect this, he used a dark slide, so constructed as to allow the plates to be immersed in different gases or liquids. A plate of silver iodide was washed and plunged into a bath of nitrite or sulphite of sodium, and exposed whilst in the solution. As a result, an image was obtained as far as A; whilst under ordinary circumstances the film was only sensitive as far as B: which, Abney thinks, proves that there exists in the silver iodide some molecular groupings which are greater, and which absorb and are reduced by red light. He sought to multiply these groups.

Certain silver bromide emulsions, absorbing the red and consequently sensitive to that light, are without any sensitiveness to ordinary modes of exposure. If they are immersed in a bath absorbing oxygen and halogen, they become as sensitive as the other. If the exposing cell contain hydrogen or nitrogen, the same results are obtained. When exposed in these conditions it is impossible to obtain a reversed image of the spectrum. This reversal, as has already been said, is

an explanation of the phenomenon of solarization, which is otherwise so difficultly explicable, and depends in all probability on the oxidation of the photographic image. And since an image on silver iodide is more easily oxidized than one on bromide, this gives a sufficient explanation of the fact that silver iodide solarizes more easily than does the bromide.

Abney prepares his emulsion by yellow light (gas light with a deep yellow glass). The emulsion is less sensitive to the yellow than to the red light.

Abney had previously found and published,* that by exposing an ordinary emulsion of silver bromide in an atmosphere of hydrogen or nitrogen, no trace of solarization (or oxidation, as he called it) of the image; consequently, by their absorption of oxygen, preservatives for dry plates impede solarization. In plates prepared with ordinary silver bromide, and exposed in solutions of pyrogallie acid, gallic acid, sulphate of iron, and ferrous oxalate in a solution of potassium oxalate, and with an alkaline developer, an image is obtained of the red and infra-red rays. In solutions of sodium sulphite, and potassium nitrite, films of silver iodide and bromide (which are without sensitiveness to the red in ordinary conditions) give, with ferrous oxalate development, an image well into the red. Certain compounds of silver thus become sensitive to certain rays through the elimination† of oxygen.‡

In terminating the examination of Abney's researches, we call to mind, that in 1857 Zantedeschi and Borlinetto (Kreutzer,

* "Photographic Journal."

† It seems, by this, that in certain circumstances red light can also exercise a reducing action, and that by means of this elimination the sensitiveness to the red can be increased.

‡ [In reviewing these last paragraphs which apply to our researches, we may say that they have been most succinctly described. There is one point which we wish to impress a little more than it has been, which is this:—It is not the silver bromide or iodide, &c., which is amenable to oxidation; it is the sub-bromide or the sub-iodide which can be oxidized. Hence, before oxidation takes place there must have been a reduction to the state of sub-salt. It may happen, and probably often happens, that in certain rays, as fast as a sub-salt is formed by them, the same rays oxidize the reduced salt, in which case the rays would, to all appearance, be said to have no effect on the silver compound. If all chance of oxidation be taken away by removal of all oxygen, then the reducing effect of these rays will be seen on development, since the oxidizing effect prevents development.—*Editor.*]

"Jahrb. Photo.," 1857, p. 460) made analogous researches. They remarked that silver iodide (by itself as well as in collo-dion) exposed to the light in a cell of nitrogen blackened more rapidly than in the air. In oxygen or in carbonic acid it coloured very rapidly (more rapidly than in nitrogen). Hydrogen also causes a reduction even in the dark.

Sahler obtained, in a remarkable manner, the same results, which he published in a very detailed work, in which, amongst other things, he put forth very curious ideas. According to him, silver chloride blackens more slowly in pure nitrogen than in oxygen, showing that oxygen aids the blackening of silver chloride by light (according to Sahler, blackened silver chloride will be an oxy-chloride (?)).

According to Sahler, not only exposure in oxygen, but in solutions of chromic acid and of permanganate of potash, aids the blackening of the silver film during development. (Compare these statements with those of Abney !)

In the preceding I have principally spoken of the manner in which silver compounds behave in light, mostly the reduction being most rapidly made by violet light. Nevertheless chemical or optical sensitizers have a considerable influence upon the progress of a process, and on the sensitiveness to light of the silver compounds.

CHAPTER VIII.

ACTION OF LIGHT ON METALLIC COMPOUNDS.

MERCURY.—The combinations of mercury are, like those of silver, chiefly sensitive to violet light. Oxide of mercury in the light decomposes into oxygen and mercury; and this takes place markedly under an uncoloured glass, less under a violet glass, and feebly under a red glass. The separation of oxygen under a red glass is five times less than under a violet glass (Dalk, 1834). Yellow oxide of mercury blackens strongly in violet light, less in white light, and still less in green light (Chastaing). Mercurous oxide, obtained by calomel and potash, takes a red colour in red light, with the absorption of oxygen; on the other hand, violet light decolorizes the red oxide of mercury.

Iodide of mercury blackens (reduction) principally in blue and violet light, and also in green light (Chastaing). It is the same with organic and inorganic salts of mercury.

Chloride of mercury, in solution in water, is decomposed in sunlight, forming mercurous chloride, hydrochloric acid and oxygen (Boullay), but, truth to say, very slowly. The presence of organic matter notably aids this reduction of the chloride. Mercuric chloride in solution in ether or alcohol evolves chlorine behind white or blue glass, but not at all behind red glass. The volatile oils distilled with water act in the same manner.

Mercuric chloride in a solution of oxalic acid is rapidly decomposed in the light. This mixture particularly absorbs the ultra-violet rays, and is decomposed preferably by them with the formation of mercurous chloride. Light, having passed through a mixture of mercurous chloride and oxalic acid, is without any action on such a mixture. Basing his ideas on these properties, Becquerel (*"La Lumière,"* p. 151) designed his actinometer. At 100° C. there was only a feeble reduction. Unfortunately, according to my researches, the

decomposition does not go hand in hand with the light. It thus follows that this mixture cannot be utilized in an actinometer. On the other hand, a mixture of mercuric chloride and ammonium oxalate can be employed for photometry. The method to be adopted I described to the Academy of Sciences at Vienna, and notified the fact in the "Bulletin de l'Association Belge de Photographie."

Mercuric and mercurous oxides in oxalic acid blacken, being reduced in blue or violet light, but do not change in red or yellow light. A solution of mercuric chloride or of mercury nitrate in ferrocyanide of potassium rapidly gives in the light (principally violet light) a greenish-blue precipitate, containing mercury. Herschel made cyanotypes in this manner; that is to say, blue prints on paper ("Phil. Trans.," 1843).

Cinnabar (particularly that obtained by the wet method) rapidly assumes a brown-black colour in alkaline solutions, and principally in ammoniacal solutions. In the presence of nitric acid, it is scarcely modified, and with water very slowly. In these mercury is not liberated, but only a modification of the sulphide of mercury is produced.

GOLD.—The oxide of gold liberates oxygen (Scheele) in the light, even *in vacuo* (Chevreul; Dingler, "Polytech. Journ.," vol. cli, p. 440). A solution of auric chloride in sunlight gives gold spangles (Scheele). Paper impregnated with auric chloride, and submitted to the action of the spectrum, is gradually decomposed. The action is seen from E to G, that is to say, from the green to the violet; the action spontaneously increases in the obscurity. The maximum action is found near G or H (Becquerel, "La Lumière," vol. ii, p. 95). Calico, silk, linen, skin, ivory, &c., behave in the same way as paper (Creutzberg, "Journ. of Pract. Chem.," vol. x, p. 880). A solution of auric chloride in ether or alcohol is bleached in the light, precipitating gold; the blue rays acting with the greatest vigour (Gehlen). The same action is found in solutions with sugar, and with gum or starch (Fischer; Kastner, "Arch. für Naturlehre," vol. ix, p. 349). Auric chloride with ammonium oxalate gives purple-red images on paper (Halleur). This mixture is also reduced little by little in the dark (rapidly by heating).

PLATINUM.—The salts of platinum behave in the light in the same manner as the salts of gold. Platinic chloride in contact with organic matter, for instance in solution in ether (Gehlen), or applied to paper, decomposes completely into metallic platinum. The bromide and iodide act in the same manner (Herschel).

Platinic chloride, mixed in lime or baryta water, gives a colourless or violet precipitate in the light, but none in red or yellow light. Johannsen carefully examined the composition of this precipitate (*"Ann. Chem. Pharm.,"* vol. clv, p. 204), and found that in all probability it is decomposed into an oxide of platinum and calcium and calcium chloride.

The reduction of platinic chloride to the metallic state is effected with difficulty by light, in the presence of oxalic acid; and the most energetic of spectral rays are the violet. A mixture of ferric chloride, oxalic acid, and platinic chloride remains unaltered, except that the ferric oxalate is reduced to ferrous oxalate, and the chloride of platinum remains unchanged. The addition of an excess of sodic oxalate dissolves the ferrous oxalate, and consequently the platinum chloride is reduced. It is this reaction on which Willis has based his new process of printing with salts of platinum (*"Photo. Journal,"* 1878). The spectrum acts on this mixture in the same manner as upon ferric chloride in a solution of oxalic acid.

COPPER.—Cuprous chloride, which has been obtained by the action of sulphurous acid on cupric chloride, or by means of zinc chloride, especially when moist, is easily decomposed in the light; the white tint passes to a dirty violet or a brownish-black (Gmelin). The body formed is probably an oxychloride of copper. If a copper plate is treated with vapour of chlorine, iodine, or bromine in the same way as a Daguerreotype plate, after exposure in the camera, and developing with mercury, an image is obtained (Schultz-Sellack; Becquerel, *"La Lumière,"* p. 68). The iodide of copper is, as a rule, less sensitive than the bromide and chloride. A polished copper plate exposed to hydrochloric acid gas, bromine, or iodine is covered respectively with cuprous chloride, bromide, or iodide, which in the light changes colour, taking a dark tint. By this means Becquerel

observed the action of the spectrum on the iodide of copper, from P as far as between H and G, but not in the less refrangible rays. The bromide of copper has two maxima: the action lies from the ultra-violet to between H and G, and attains a maximum there; remains constant as far as G, and ascends again to a new maximum about D. The action shows itself as far as A. The chloride of copper behaves in the same manner, only the first maximum is found in the ultra-violet, whilst the second one is reached about D. The iodide is much less sensitive to the green, yellow, and red than the bromide or chloride. A solution of cupric chloride in alcohol or ether is decolorized by light (Gehlen, Neumann), and is decomposed into cuprous chloride by the addition of water. I found red or yellow light almost without action on this mixture. The double oxalate of sodium and copper (cupricum) is sensitive above all others to light in the presence of a ferric oxy-salt. Similarly the double salt of ammonium (Weiske, "Phot. Arch.," 1864, p. 262), and the double tartrate of potassium and iron (ferricum), in the presence of a copper salt (Ehrmann), deposits metallic copper in the light.

It appears rather doubtful if the violet rays play the greatest part in the action. A mixture of cupric chloride, ferric chloride, and hydrochloric acid applied to paper gives in the light, firstly, ferrous chloride, and afterwards cuprous chloride.*

LEAD.—The carbonate of lead, heated to redness, gives a yellow oxide of lead. Spread in the form of a powder on paper, this oxide darkens under blue glass, and remains yellow under red or yellow glass; whilst, on the other hand, a paper somewhat darkened by light is decolorized under yellow or red glass (Becquerel, "La Lumière," p. 56). The plumbous oxide, in the presence of an alkali and water, becomes oxidized and converted to minium (Levol, "Ann. Chem. Phys.," vol. xlvii, p. 196). The binoxide is reduced by light to minium. In this reduction red light acts more rapidly than

* Obernetter ("Phot. Arch.," 1864, p. 77) has based a printing process on this reaction. The spectrum seems to act upon the ferric chloride alone; at the same time the violet end is particularly active.

violet light (Davy). Iodide of lead, exposed for a long time to green or violet light, preserves its yellow tint, and is not visibly altered. It has, nevertheless, a tendency to reduction; for instance, mixed with starch, it becomes blue more rapidly than that which has been kept in the dark or in red light (Chastaing). According to Schmitt ("Phot. Mitt.," vol. iii, p. 238), iodide of lead in the dry state is not acted on by light; it only decomposes in the moist state, and in contact with air; there is then an elimination of iodine, and the production of oxide and carbonate of lead. Chloride of lead remains unaltered by light. Sulphide of lead, precipitated on paper, gives an image in the light. The illuminated portions oxidize rapidly, and become decolorized. It is not yet ascertained if the red rays have the most action.

CHAPTER IX.

ACTION OF LIGHT ON IRON SALTS.

FERROUS SALTS.—The ferrous salts are reduced as rapidly by light as by heat. Ferrous sulphate oxidizes more rapidly in contact with air and red light than in the dark, and the purely chemical action, when shaded from light, is greater than oxidation in presence of violet light, which has a reducing action. Chastaing examined the oxidation of ferrous sulphate during periods of from one to five days in light of different colours. The oxide formed was ascertained volumetrically, the oxidation in darkness being 1. The following figures show the other relative rates of oxidation :—

	A	B	C	D	E
In darkness ...	1'00	1'00	1'00	1'00	1'00
Red light ...	1'48	1'55	1'80	1'25	1'21
Violet light ...	1'15	1'39	—	1'45	1'58
Green light ...	—	—	1'66	1'90	1'86

The ferrous hydrate does not give very exact or definite numbers. Here, again, the reducing action of the violet exceeds that of the red (Chastaing).

FERRIC SALTS.—The ferric salts, in presence of organic matter, are reduced by light. A solution of ferric chloride, brushed on paper, is sensitive to the light : it is reduced to ferrous chloride.

A solution of ferric chloride in ether passes into the ferrous state when exposed behind blue or white glass, and not behind yellow or red (A. Vogel). According to Chastaing, the violet rays are those which reduce solutions of ferric chloride in ether to the ferrous chloride with the greatest rapidity. In the dark, as well as in yellow or red light, a little ferric oxide separates. Döbereiner found, in 1831, that an aqueous solu-

tion of ferric oxalate was decomposed into carbonic acid and ferrous oxalate by sunlight and by blue or violet light, but not by red or yellow light (Schweigger, "Journ.," vol. lxii, p. 92).

Suckow, in 1832, found that the action of light on ferric oxalate, after passing through a violet glass, was the same as that of white light; that the action was retarded by a blue glass, and still more by a green. In yellow or red light he remarked no change. Applied to paper, ferric oxalate is sensitive to the green to a notable degree beyond the visible violet of the spectrum.

Reynolds ("Brit. Journ. of Phot.," 1861, p. 9) compares the relative action of the solar spectrum on paper impregnated with ferric oxalate with that of silver chloride. He found that the action of light was nearly the same as that on silver chloride. According to my researches, ferric oxalate is relatively more sensitive to the green than silver chloride. A mixture of ferric chloride and oxalic acid, or of oxalates, behaves in the same way. It is also the same when double oxalates of iron (ferricum) and ammonium, sodium, or potassium are used. The presence of free hydrochloric acid does not hinder the reduction by light. According to my researches, such mixtures can scarcely be surpassed by any other in their sensibility to direct light. Reynolds ("Brit. Journ. Phot.," 1861) and Phipson ("Phot. News," 1862) published, independently of each other, printing processes with oxalates of iron.*

The image is formed by insoluble ferrous oxalate, and can be intensified by gallic acid (black image), potassium, ferricyanide (blue image), auric chloride (ruddy-brown image), or by means of potassium permanganate (brown image).

Actinometers made by means of ferric oxalate give a measure of the ultra-violet, violet, blue, and blue-green rays. The same rays are measured by means of ferric chloride and oxalic acid. Marchand ("Etude sur la Force Chimique," 1875) examined the action of the spectrum on a mixture of ferric chloride and oxalic acid, with which he had filled his photometer. He measured the action of the different

[* It must not be forgotten that Dr. J. W. Draper was the first who produced a print with ferric oxalate.—*Editor.*]

rays by the quantities of carbonic acid eliminated during equal times. He found as follows :—

In the red rays	5'7
„ orange rays	9'9
„ yellow rays	43'1
„ green rays...	134'1
„ blue rays	615'8
„ indigo rays	370'0
„ violet rays...	321'0
„ ultra-violet rays	52'1

The work of Marchand showed—1st, that oxalic acid allows all coloured rays to pass; 2nd, that the ferric chloride only allows the red, orange, yellow, green, and a very little blue to pass; 3rd, that a mixture of the two only allows the red, orange, yellow, and green to pass, without a trace of blue. The intensity of luminous action was determined by a quantitative determination of the ferrous oxide produced,* or by the quantity of carbonic anhydride disengaged during oxidation of the oxalic acid.†

In this method the absorption of the carbonic acid by the liquid must be taken into account, the absorption being variable with temperature and pressure; besides which, for small quantities, the process does not give regular results. In all actinometers hitherto constructed, this has not been sufficiently taken into account; and, in spite of all the favourable notices, their indications must be considered doubtful.

As long ago as 1842, Herschel utilized ferric citrate to obtain images by the action of light. Ferric chloride, mixed with citric acid, is much less sensitive than the mixture with

* Draper (1857) decomposes the solution, after exposure to light, by chloride of gold. The ferrous oxide thus formed precipitates metallic gold, which is weighed. He prefers this method to the measurement of carbonic acid ("Dingler," vol. cxlvi, p. 29).

† According to Lepowitz and Woods ("Phot. Arch.," 1864), employed later by Marchand, as an actinometer, in a long series of researches ("Phot. Mitt.," vol. xi, p. 142). Becquerel ("Fort. Phys.," 1874) contests the accuracy of Marchand's process, who, in his turn (1874) defends his method against the criticisms of Becquerel, and says that he did not wish to determine the chemical intensity of light, except so far as it had acted on the liquid ("Ann. Chem. Phys.," [5], vol. ii, p. 160).

oxalic acid, and the process does not proceed so well as with the oxalic acid; at the same time, whilst a little carbonic acid is formed, variable quantities of acetic and oxalic acids are also formed. Ammonio citrate of iron (ferricum), brushed on paper, is reduced under the action of the solar spectrum, from the violet as far as blue-green to near F (Draper). A mixture of this salt and potassium ferricyanide rapidly becomes blue in the blue, in the violet, and in the ultra-violet; but by prolonged action these rays destroy the colour. The blue rays, above all others, produce this decoloration with great rapidity (Herschel).

The reduction of the ferric citrate, and its double salt, with ammonium citrate form the basis of the chrysotype, or aurotype,* and the cyanotype.† These salts behave like the oxalate compounds. Images in carbon can also be obtained.

A mixture of ferric chloride and tartaric acid exposed to white light and to coloured light, in the same manner as the organic salts of iron already described, is less sensitive than the oxalate. In the light, ferrous tartrate and ferrous chloride are formed with difficulty, and can be employed in photography like the oxalate. Poitevin made use of it for photographic purposes ("Compt. Rend.," vol. lii, p. 94). The portions not acted upon by light, for instance on paper, possess a variety of properties; they are not crystallizable, and not hygroscopic, whilst in sunlight they dissolve and become hygrometric from ferrous chloride. By the application of coloured powder an image is formed, by its adhering only to the hygrometric portions. Gum, glue, and albumen are rendered insoluble by the ferric oxide becoming soluble in the light, by the formation of ferrous salts. On these facts Poitevin based different pho-

* Paper sensitized with ammonio-citrate of iron, after prolonged exposure, is plunged in a bath of auric chloride or a solution of silver. On most parts reduced by light, metallic gold or silver will be deposited (Herschel, "Athenæum," 1842, p. 748).

† The ferrous oxide produced is rendered visible by an application of red prussiate of potash (potassium ferricyanide). The image appears blue where the light has acted. The ferricyanide can also be added, to begin with. The yellow prussiate (potassium ferrocyanide) makes the unexposed portions visible.

tographic processes.* The portions altered by light also condense mercury vapour (Merget).†

Ferric sulphocyanide in aqueous alcoholic or etheric solution, which is of a beautiful red colour, is reduced to the ferrous sulphocyanide, according to Grotthus, principally by the blue-green rays. In light, in a closed flask, the decoloration proceeds rapidly; but the solution becomes red when in contact with the air.

* Coloured gelatine is altogether insoluble in a mixture of tartaric acid and ferric chloride, but becomes soluble on exposure to light. Thus, it is possible to work with this in the carbon process, as it is with the chromates. The exposed portions repel greasy printing ink, whilst it takes on the non-exposed portions. This is the basis of Poitevin's new phototype process ("Bull. Société Française," 1878).

† A mixture of ferric chloride, tartaric acid, and platinum chloride, exposed to light, produces ferrous chloride; the portions exposed condense mercury vapour, which reduces the salt of platinum ("Bull. Soc. Fran.," 1872).

CHAPTER X.

ACTION OF LIGHT ON THE SALTS OF URANIUM, VANADIUM, &c.

URANIUM.—The salts of uranium behave like the salts of iron: they are deoxidized in the light; but to be so they require the presence of organic substances—alcohol, ether, glycerine, collodion, &c. (Nièpce, 1858). A solution of uranium nitrate in alcohol diluted with water is only reduced by the blue and violet rays; the red and yellow are without action. Aldehyde and acetic acid are formed as secondary products (Chastaing). The reduction of uranic nitrate to the uranous salt also takes place with other organic matter, such as paper. On this fact Burnett, in 1858, based a photographic printing process. The tartrate and oxalate are particularly sensitive to light. The photographic image, amongst other ways, can be intensified by silver nitrate or auric chloride. With potassium ferricyanide they become red; and green with salts of cobalt. Nièpce (Dingler, 1859) has studied this process from a photographic, and he, Corvoisart, and Lukamp from a chemical, point of view ("Ann. Chem.," vol. cxiii, p. 114, and vol. cxxii, p. 113). In 1851 Burnett constructed an actinometer of oxalate of uranium ("Phil. Mag.," 1859), and perfected it in 1860. Recently, Monckhoven published a description of a photometer made with ammoniacal oxalate of uranium. He utilizes Wood's apparatus, and endeavours to determine the action of light by the gaseous products. In this method he did not take possible errors sufficiently into account. (See the criticism of Dr. Eder at the meeting of the Photographic Association of Vienna, 8th October, 1879.) In this case also the blue and violet rays are principally active.

CHROMIUM.—Chromic chloride is decolorized in the light, and gives images with less oxidizable metallic salts (Monck

hoven). The salts of chromium are by themselves stable in the light; but, in the presence of organic matter, a reduction to the state of chromo-chromic oxide, and finally to chromic oxide, takes place. The alkaline bichromates (and also the chromates of copper, lead, and silver) are the most sensitive to light in the presence of gelatine, dextrine, gum, alcohol, &c. I have found that similar mixtures darken in the violet, blue, or green of the spectrum, and do not change in the red and the yellow. Paper prepared with potassium bichromate, according to Becquerel, changes colours most about the ray F, at the extremity of the green; near *b* and E the action is suddenly stopped. By a prolonged exposure it is possible to register the Fraunhoferic lines ("La Lumière," vol. ii, p. 95). According to Draper, the action goes from the violet to the yellow, near the line F. The bichromate of copper, or a mixture of bichromate of potash and sulphate of copper on paper, by a partial reduction of the salts of chromium, forms a neutral insoluble chromate of copper (Burnett, "Phot. Journal," 1858). The action is due to the blue and violet rays. A mixture of bichromate and ferrocyanide of potassium changes, in the light, to an oxide of chromium and ferricyanide of potassium. Hunt utilized such a mixture on paper for a chromo-cyanotype process ("Phil. Mag.," 1844, p. 435).

Mixtures of the chromates and organic substances are more sensitive to the direct action of light than silver-chloride paper. If, for instance, on the one hand, silver-chloride paper is exposed till the usual black is obtained, and, on the other, carbon paper till a good image is produced, it will be found that the chromated paper with gelatine only requires from one-third to one-sixth of the exposure necessary for the silver-chloride paper. It follows that the chromate processes can be used in bad light, such as in the dark winter days. Above all, this shows that this process is less dependent on the ultra-violet rays than is the chloride-of-silver process. On dark days there are very few ultra-violet rays. Watery vapour blocks them out, and in the morning, or when the sun is covered with clouds, only a feeble quantity of the violet end of the spectrum can pass through; whilst, under the same conditions, red, yellow, and even green light is but little diminished in intensity (Janssen, Roscoe, H. W. Vogel). In such a case chloride-of-silver paper prints less rapidly than

chromated paper ; the violet rays, which have the most energetic action on it, are in defect, whilst the blue, which are the rays which act most powerfully on the chromate, are less so. On this account, actinometers of silver chloride paper, for the control of printing on carbon tissue, are not to be recommended.

All the known practical chromate processes so far rest on the property that bichromate of potash possesses of rendering organic substances, such as gelatine, gum, albumen, dextrine, sugar, &c., insoluble in light, with the production of chromic oxide. These processes are represented by the carbon, photolithographic, photo-galvanic, and the powder processes. At the present time bichromate of potash is frequently used for the manufacture of actinometric paper (H. W. Vogel, "*Lehrbuch der Photo.*").*

VANADIUM.—Vanadic acid behaves like chromic acid (Gibbons, "*Phot. Corr.*," 1876, p. 159).

MOLYBDENUM.—Molybdic acid is coloured blue in the light, when in the presence of organic matter. A solution of molybdic acid, in sulphuric acid, becomes blue in sunlight, but only in the presence of organic matter (Phipson, "*Phot. Arch.*," 1863, p. 249). Later ("*Chem. News*," 1874, p. 33), Phipson again recommended this as an actinometer.

MANGANESE.—The manganate of potash is sensitive to light, and gives positive images on paper, as does a solution of the permanganate in cyanide of potassium (Monckhoven). The red aqueous solution of oxalate of manganese is decolorized by sunlight, but more gently in violet and blue light, with the formation of manganous oxalate and carbonic acid (Dorbereiner).

Manganous hydroxide oxidizes most rapidly in the red light

* For fuller details as to the reduction of the chromates, and also as to the scientific principles of modern chromate photography, see my memoir recently honoured by the Photographic Association of Vienna, "*Les réactions de l'acide chymique et des chromates sur les substances organiques dans leurs rapports avec la chromo-photographie*," Vienne, 1878.

and in the air. In darkness, or in green light, the oxidation goes on less rapidly than in red light; more gently in the violet light, whose action is a reducing action. If the value of oxidation in the dark be equal to 1, according to Chastaing, in different coloured lights the following rates are obtained:--

		A	B
In darkness	...	1'00	1'00
„ red light	...	1'18	1'38
„ green light	...	—	'98
„ violet light	...	'57	'57

CHAPTER XI.

ACTION OF LIGHT ON THE IODIDES, &c.

POTASSIUM IODIDE splits up into potassium hydroxide and iodine in the light (Loew., "Fortschr. der Phys.," 1869, p. 413). The presence of carbonic acid and air favours the decomposition (Battandier). In the presence of sugar, potassium iodide rapidly becomes yellow (Durewell, "Chem. Centralblatt," 1876).

AMMONIUM IODIDE is sensitive in the same degree. Blue light acts strongly on the iodides, and yellow light but very feebly.

HYDRIODIC ACID is split up into iodine and hydrogen under the influence of the most refrangible part of the spectrum (Lemoine, "Pog. Beib.," vol. i, p. 510). In 1879 Leeds constructed a photometer with potassium iodide and weak sulphuric acid. He calculated the amount of iodine set at liberty by the action of light, by testing with sodium hyposulphite.

An aqueous solution of iodine does not change in the light (Vogel, "Phot. Cor.," 1866, p. 62). The blue solution of iodide of starch in water is completely decolorised by white light, and by the yellow and green rays of the spectrum. The red and blue rays act feebly, and the violet rays are without action; so much so, that the reverse to this, the decoloring action, progresses in daylight.

BROMINE AND CHLORINE.—Bromine water behaves like chlorine water. The gaseous chlorine preferably combines with another body in the presence of light, and principally in the blue and violet, whilst the red and yellow do scarcely, if at all, influence it.

This is notably the case in a mixture of chlorine and

hydrogen, which in the light (in bright light, and with explosion) combine to form hydrochloric acid. The maximum action of the solar spectrum is between G and H (Fabre and Silbermann, "Ann. de Chem.," vol. xxxvii, p. 297). In the indigo, according to Draper, the action is the most intense, the light then acting 700 times more energetically than in the ultra-red. Bunsen and Roscoe have found two maxima in the spectrum, the first between G and H, whence the action diminishes to about H, then increases as far as the ray I in the commencement of the ultra-violet, and then is *nil* in the ultra-violet; thus, before arriving at the spectrum, rendered visible by fluorescence, the action becomes inappreciable ("Pogg. Ann.," vol. cviii, p. 267). The results obtained by Bunsen and Roscoe are to be found in the accompanying table. The figures giving the action in the different regions of the spectrum are compared to the quantity of hydrochloric acid formed in one minute, which are quantities measured according to the unit of the instrument. The indication of the region gives the limits of the rays passing through the slit. Thus C — $\frac{1}{2}$ DE means that the slit allows a bundle of rays limited on one side by the C line, and on the other by a line midway between D and E; $\frac{1}{5}$ DE — F means rays commencing at $\frac{1}{5}$ of the distance between E and D towards D, and ending near F.

C — $\frac{1}{2}$ DE	...	0.5	H — $\frac{3}{4}$ IM	...	55.1
$\frac{1}{5}$ DE — E	...	1.3	$\frac{4}{5}$ OM — N	...	38.6
$\frac{3}{4}$ DE — F	...	1.4	N — $\frac{3}{4}$ QR	...	18.9
$\frac{1}{5}$ FG — G	...	28.4	$\frac{1}{2}$ NQ — $\frac{1}{3}$ RS...	...	12.5
C — $\frac{4}{5}$ GH	...	54.5	$\frac{1}{2}$ RS — $\frac{2}{3}$ ST...	...	2.1
$\frac{1}{5}$ GH — H	...	60.5	$\frac{3}{4}$ ST — $\frac{2}{3}$ UV	...	1.2
$\frac{3}{5}$ GH — I	...	52.7			

Bunsen and Roscoe, in measuring the absorption of chlorine, showed that the chemical action of light followed in the wake of the absorption, that is to say, of the passage of a certain quantity of energy in the movement of the ether on the molecules of the body, although this absorption took place without chemical action; and was comparable to the mixture of chlorine and hydrogen, when the light causes, at the same time, the combination of the gases to the state of hydrochloric acid.

The co-efficient of extinction of a mixture of equal volumes of gaseous chlorine and air = $\frac{1}{346.6}$. The co-efficient of extinction of equal volumes of gaseous chlorine and hydrogen is $\frac{1}{284}$. This latter, which is much larger, proves that the chemical action requires a quantity of light proportional to its density. The difference between the two gives the co-efficient of chemical extinction = $\frac{1}{723}$. This proves that, whereas in the detonating mixture of chlorine and hydrogen the light is simply utilized by the chemical action, and that it produces no other movement, the light of the source utilized for the experiment was diminished by one-tenth in its chemical action by passage through a layer of a thickness of 723 millimeters; for other luminous sources, giving light otherwise composed, this number would be evidently something else.

Chlorine decomposes water in the light, with the formation of hydrochloric acid, oxygen being disengaged. In the same way chlorine more readily decomposes organic hydrocarbons in the light.

Marsh-gas and ethylene do not unite with chlorine in the dark, but rapidly in diffused light. In sunlight the combination is so violent that it is explosive (Regnault and Laurent, "Ann. Chem. et Phys.," (2) pp. 60 to 71). Chlorine behaves in the same way with benzine and naphthaline in the presence of light. This is also the case with other substances, such as ether, alcohol, acetic and prussic acids, all of which combine with chlorine more readily under the action of light. Bromine and iodine present the same phenomena, but in a more feeble degree.

NITRIC ACID.—Concentrated nitric acid is decomposed by light into oxygen and nitrous acid, and at the same time is coloured yellow: this takes place under white, blue, or violet glass, but not under red glass (Seebeck).

PHOSPHORUS.—White phosphorus in water or in different gases is rapidly changed in sunlight or violet light into red phosphorus. In red light this modification takes place but slowly (A. Vogel; Sweigger, "Journ. für Chem. und Phys.,"

vol. vii, p. 95, and vol. ix, pp. 23 *et seq.*). According to Schrötter, heat produces the same effect. Draper demonstrated in a very simple manner the sensitiveness to light of white phosphorus in its passage into the red modification. He flowed a thin film of phosphorus between two pieces of white glass, and exposed it to the spectrum. He afterwards dissolved away the white by carbon disulphide, which left the red intact. Draper thus obtained a photographic image of the most refrangible parts of the spectrum.

SULPHUR.—A concentrated solution of sulphur in carbon disulphide, exposed to light, deposits yellow insoluble sulphur. The light, having passed through the solution, is found to have been deprived of the rays between H and G, and the ultra-violet of the spectrum is completely absorbed (Lallemand).

POTASSIUM FERRICYANIDE, in an aqueous solution, is completely reduced by light to the state of ferrocyanide (together with a blue body). The decomposition is due to the blue or violet rays, and not to the yellow (Herschel, "Phil. Trans.," 1842). The presence of organic substances, such as paper, helps the reduction. For an aqueous solution the reduction is found to be twice as strong in the violet as in the yellow (Chastaing). The presence of gelatine (as is the case with bichromate of potash) aids enormously in the decomposition by light of ferricyanide (Gintl, "Chem. Centralbl.," 1871, p. 591). Ferricyanide of potassium applied to paper is also sensitive; it changes principally to ferrocyanide. The salt reduced by the light can be rendered visible by the application of ferric chloride, of nitrate of uranium ("Lexicon," p. 154), of silver nitrate, and of the salts of cobalt (Burnet, "Phot. Not.," 1858). I have found that a mixture of ferricyanide and of a solution of ammonium oxalate is more sensitive than the first-named body by itself; it forms a bluish precipitate. Ferricyanide and ferric chloride give, gradually, in the solution a precipitate of prussian blue; according to my researches, the sensitiveness to green or blue light does not appear to differ so much as for silver chloride, or even as the oxalate of iron: both of these, and principally the latter, decompose much more rapidly in the light than the above mixture. Red or yellow light only act very feebly on it. According to Herschel, all the visible

spectrum acts on it, but principally the blue and the violet; from the yellow to the ultra-red the action is only feeble.

A solution of potassium, ferricyanide, and of corrosive sublimate rapidly becomes turbid in white light, but not under a red or yellow glass, giving a bluish-green precipitate; in the first place the mercuric chloride is reduced to mercurous chloride, or calomel. Mixtures of solutions of potassium, ferricyanide and of the nitrates of lead or uranium become slowly turbid in the light; the first give a light blue precipitate, the second a brown precipitate. The reduction of the ferricyanide continues; coloured light acts on such mixtures as indicated above.

PRUSSIAN BLUE is decolorized in sunlight with the formation of cyanogen, and also *in vacuo* (Chevreuil). In the dark the blue colour reappears, oxygen at the same time being absorbed (Graham-Otto, "Chem.," 1872, p. 1203). Red light acts principally on prussian blue (Baudremont, "Phot. Corr.," 1878, p. 173). A solution of prussian blue in oxalic acid, according to Scheras, gives, in the light, insoluble prussian blue; but Böttger ("Chem. Central.," p. 182) denies this.

SODIUM NITRO-PRUSSATE.—Aqueous solutions of sodium nitro-prussiate give in the light a blue precipitate; upon paper a very feeble blue image is obtained, which can be intensified by means of ferrous sulphate. A very peculiar action is that of coloured light on a paper prepared with silver chloride and an excess of silver nitrate, and then plunged into a solution of nitro-prussiate. Such papers give natural colours with a vigour dependent on the excess of silver nitrate. When free silver nitrate is absent, merely a black and white image is obtained, and no reproduction of colour (Brakenbridge, "Zeitsch. Phot.," 1861, p. 128). In the light, and most probably under the influence of the violet end of the spectrum, a mixture of sodium nitro-prussiate and ferric chloride gives prussian blue; at 100° C. there is no decomposition. According to Roussin ("Phot. Arch.," 1865, p. 342), sunlight precipitates a quantity of prussian blue proportional to the exposed surface and to the intensity of the light. This quantity can be collected, dried at 100° C., and weighed. This mixture can be employed as an actinometer; according to my experiments, the truth is, this is more sensitive to light than a mixture of potassium

ferricyanide and ferric chloride, but less so than the ferric oxalate. In the absence of free acid the sensitiveness is a little greater. A. Vogel has established ("Phot. Arch.," 1871, p. 92) that a petroleum lamp—a strong light, but deficient in violet and ultra-violet rays—gives, after twenty-four hours, a blue coloration, but not an appreciable precipitate; while a magnesium light, rich in ultra-violet rays, causes the decomposition in a very short time.

ARSENIC.—Metallic arsenic, in a concentrated solution of caustic potash, is oxidized in the air, giving potassium arsenite. These experiments were made with gaslight—a light rich in yellow and red rays, poor in blue and violet, and giving in consequence results more pronounced for the red. The oxidation to the state of arsenic acid is shown in the following table:—

	A	B	C	D
In the dark ...	1'00 ...	1'00 ...	1'00 ...	1'00
„ violet ...	1'00 ...	0'98 ...	0'92 ...	0'93
„ red ...	1'04 ...	1'06 ...	1'10 ...	1'20
„ green ...	— ...	— ...	— ...	—

In the same way as with the salts of iron, the violet rays have a reducing action,—that is to say, retard oxidation. The red oxidizes; the green is indifferent. Arsenic acid in a dilute solution of caustic potash is oxidized, and becomes arsenic acid. It may be stated, that after several days' action the minimum oxidation takes place in the violet, and that the maximum is due to the red, although the difference is small.

SULPHIDES.—A very dilute solution of sulphuretted hydrogen in water is scarcely more decomposed in violet light than in the dark, whilst red light decomposes it more rapidly by oxidation.

The mono- and poly-sulphides of sodium give, in different coloured lights, a variable quantity of sulphur and hyposulphite: the decomposition is almost equally active in the green, in the violet, and in the dark; red light is most favourable for oxidation.

SULPHUROUS ACID, under the influence of violet light, is changed to sulphuric acid (thus an oxidation in the violet appears contrary to the laws laid down by Chastaing). But if this reaction takes place in a vacuum and in the presence of free sulphur, it is seen that the light first commences to reduce the sulphurous acid to the state of sulphur and oxygen, which afterwards oxidizes the sulphurous acid.

CHAPTER XII.

ACTION OF LIGHT ON ORGANIC COMPOUNDS.

ORGANIC MATTER.—This is decomposed, and generally combines with the greater facility under the influence of light than in its absence. Light principally favours oxidation. Many colouring matters bleach in the light by oxidation. It is thus that the bleaching of such organic matters as saffron, indigo, logwood, turmeric, &c., are explained. Colours are ordinarily distinguished as permanent or fugitive colours according to their resistance to exposure to the air. There is not in reality any absolutely fixed organic colour; for all undergo change in the light, but some more slowly and feebly than others. Certain pigments bleach in the light, and take a deeper tint in the dark, as very exact comparative experiments have shown (A. Vogel). In 1857 Chevreuil read to the Académie de Science of France a work in which he proved that the bleaching of organic colouring matter by light required not only the intervention of oxygen, but also that of light; the colours resisted change equally as well in the light in a vacuum as in the air in darkness ("Compt. Rend.," 1854 and 1858).

Light particularly acts on vegetable colours, and in a manner varying with each colour. Nearly every ray can act. Thus the rays from the green, as far as the violet, bleaches the yellow stain of the yellow crocus pressed on paper. In the same way the red and yellow change the rose-red colour of the stock; the rich blue of the scented violet, which carbonate of soda makes green, is bleached by the same group of rays. The green colour of the leaves of the elder is changed by the ultra-red. These examples show that every part of the spectrum is active in effecting changes, and that certain vegetable colours are influenced by certain rays, and other colours by other rays (Herschel, "Phil. Trans.," 1844). The leaves of the *Papaver Rhæas* flower decolorize more rapidly under a blue

than under a white glass (A. Vogel). According to Herschel, the colours of flowers bleach most rapidly in the colours complementary to them; thus the colouring matter of yellow flowers fades in blue light, that of violet in the green, of blue in the yellow-red, of the rose and purple in the yellow and in the green. There are very few exceptions to this rule.

Colours derived from coal tar (aniline colours) are very sensitive to the light, in which they rapidly bleach. According to Tóth and myself, we have found that with chrysoidin and anilin red this bleaching is principally due to blue and violet light; for if paper dyed with these colours be exposed under a yellow-green glass, allowing neither blue nor violet to pass, or under a red glass, this remains unaltered for a year, whilst the colour rapidly disappears in daylight. The colours of the wings of butterflies principally bleach in white or violet light: of all the spectrum rays these last act most energetically (Capronnier, "Phot. Mit.," vol. xiv, p. 50).

CYANINE-BLUE is sensitive to yellow light. It absorbs strongly the part of the spectrum—that is to say, the yellow—to which it is most sensitive. (*Vide ante.*) Turnsol oxidizes strongly in the violet, less in the red, and very little in the dark (Chastaing). According to other observations, yellow should have the strongest action on turnsol.

OILS oxidize slowly in the air; this oxidation is accelerated by heat and light. The blue and violet rays act with greater energy than the less refrangible rays (Cloeze, "Compt. Rend.," 1865, pp. 321 and 981).

Linseed oil, prepared with litharge, oxidizes in the light, and becomes insoluble in ether and oils (Labord, "Bull. Soc. Phot.," 1858).

Amongst the essential oils are hydrocarbons, the oxidation of which is strongest in violet light, next in the red or green; the oxidation is very feeble in obscurity (Chastaing).

The OIL OF TERE BENTHIN gives by oxidation the following results:—

		A		B		C		D
In the dark	...	1'00	...	1'00	...	1'00	...	1'00
„ red	...	2'36	...	1'94	...	2'30	...	2'00
„ violet	...	2'57	...	2'98	...	2'66	...	3'00

According to these experiments, violet light acts with the greatest energy.

The OIL OF LEMON gives the same results as terebenthin. The oxidation is—

			A		B
In the dark	1'00	...	1'00
„ red light	2'23	...	1'41
„ green light	2'43	...	1'44
„ violet light	3'14	...	2'05

The oil of lemon absorbs oxygen more slowly than the oil of terebenthin, though the rate of absorption under the influence of coloured light is the same.

XYLENE.—In this case the maximum absorption is also in the violet; least in the dark. Exposure was given from two to eight days.

ALDEHYDES.—The oxidation of the aldehydes progresses more slowly in the dark than in the light. In summer; in the dark, about one; in the yellow, two; in the violet, three. Chastaing found the following numbers:—

			A		B		C
In the dark	1'00	...	1'00	...	1'00
„ red	1'28	...	1'88	...	1'50
„ violet	1'53	...	2'72	...	2'33

The OIL OF CINNAMON oxidizes more slowly than aldehydes. It oxidizes in about eight days.

				A		B
In the dark	1'00	...	1'00
„ red	1'10	...	1'81
„ violet	2'17	...	2'45

OIL OF BITTER ALMONDS.—In from three to twelve days the oxidation was—

				A		B		C
In the dark	1'00	...	1'00	...	1'00
„ yellow	1'44	...	—	...	—
„ violet	3'00	...	1'50	...	1'66
„ red	—	...	1'13	...	1'30
„ green	—	...	1'33	...	1'35

ETHER.—Ordinary ethylic ether oxidizes rapidly in the violet, a little in the red, and very slowly in the dark.

In the dark	1'00
„ red	1'20 to 1'40
„ violet	2'50 to 3'50

PHENOL becomes red in the light, particularly in violet light, on account of the oxidation of its impurities.

MINERAL OILS, under the influence of light, absorb oxygen and transform it into ozone, which easily oxidizes the bodies with which they are in contact (Grotkowsky, "Bull. Soc. Chim.," 1869 [II], p. 75; "Dingler," vol. cxc, p. 173). It may here also be supposed that violet light has the predominant effect.

The TINCTURE OF ALOES, originally a yellowish red, becomes gradually blood-red by oxidation under the influence of violet or blue light, whilst the red rays produce no alteration in it (Marbach, "Phys. Lexicon," vol. iv, p. 847).

ASPHALTUM AND RESIN.—If a thin film of a solution of these substances in alcohol, ether, or essential oils be exposed to light, the parts so exposed, according to old theories, become oxidized and insoluble. According to the researches of Kayser ("Phot. Cor.," 1879, Sept.), the insolubility is not only caused by oxidation, but also by an alteration in molecular condition. Asphaltum gives a spectrum image from A to H, or through the whole visible spectrum. Caoutchouc (according to Swan, "Phot. News," 1872) and santonine (Vogel, "Lehrb. Phot.," p. 21) equally change in the light.

GUM GUIACUM powdered, or spread by an alcoholic solution on paper, is coloured green in white or violet light (oxidation), and in yellow or red light regains its original colour (Wollaston; Herschel). Without the presence of air, for instance, in an atmosphere of hydrogen, guiacum does not colour green in the light. The green coloration arises from the formation of a blue insoluble body in alcohol, in the substances still undecomposed (Biot, "Compt. Rend.," vol. viii, p. 598). Paper impregnated with an alcoholic solution of guiacum is coloured a yellow-green in a mixture of chlorine and air; the spectrum prints the natural colours, except the green. The colours

rapidly disappear (Herschel, Photochromie, "Phil. Trans.," 1868, vol. xvii, 1842). The maximum action is about M. A guiacum paper coloured blue by chlorine water, and afterwards receiving the image of the spectrum, is decolorized from the red to the violet, with a maximum action about F. This phenomenon is a deoxidation. Guiacum paper is not coloured, if the ultra-violet light is cut off from H, by allowing light to pass through a solution of quinine. In the spectrum it becomes blue from H to P (Becquerel).

SULPHATE OF QUININE cuts off those rays which produce fluorescence,* particularly the ultra-violet, producing a molecular change, and is transformed into sulphate of quinidine.

TURMERIC similarly is most acted upon by the rays which produce fluorescence. Turmeric paper is decolorized by oxidation under a violet or green glass, and remains unaltered under a red glass (Chastaing). Turmeric paper is modified in the light, even when its colour is not actually changed. Dilute lime-water does not darken paper which has been exposed to light, although this same solution gives an apparent reaction with this paper when shaded from light (A. Vogel, "Phot. Arch.," 1871, p. 97).

AMYL-NITRITE, according to Tyndall, is decomposed in the light, especially when a beam of light is allowed to pass through its vapour. In the interior of the beam a thick cloud of amyl-nitrate, hyponitrite, and other products are formed. The blue rays have the greatest action. The light which has passed through the vapour of amyl-nitrite is without any effect on this body. Ethyl-nitrite behaves similarly.

Light is almost without any action on the formation of ether. This feeble action becomes *nil* with time, even before the etherification is complete.

CHLOROPHYLL is the green colouring-matter of leaves. Solutions of chlorophyll are oxidized in the light, and decolorize, and this in a varying degree, according to the nature of the solvent.

[* It would perhaps be more accurate to say, which usually produce fluorescence, since there are bodies which fluoresce when excited by rays in the visible spectrum.—*Editor.*]

Chlorophyll in the following solvents is decolorized in the light, thus—

Chlorophyll dissolved in alcohol		at 75°	in '05 hour.
"	"	benzene	" '11
"	"	ether	" '20 "
"	"	olive oil	" 3'50 hours.

Chlorophyll is most rapidly oxidized by the rays which it absorbs; that is to say, by the orange-red rays. Dilute solutions decompose more rapidly than concentrated ones (Gerland, "Fortschr. der Phys.," 1871, p. 468; 1872, p. 433. Wiesner, *loc. cit.*, 1874, p. 609). As a rule, an alcoholic solution of chlorophyll behaves in the spectrum almost inversely to that of silver chloride. Cossa ("Deutsch. Chem. Gesell.," 1874, p. 358) exposed such a solution to one part, and chloride of silver to another part, of the spectrum—in one case under a solution of potassium bichromate, and in another beneath an ammoniacal solution of cupric sulphate. In the first case the chlorophyll was bleached, and the paper scarcely changed. In the second case, the chlorophyll remained unaltered, and the silver chloride became black.

XANTHOPHYLL.—According to Wiesner, is rapidly decolorised by the rays which pass through ammoniacal cupric sulphate: green, yellow, or red light has no action.

CHAPTER XIII.

ACTION OF LIGHT ON PLANTS AND ANIMAL LIFE.

PLANTS.—It was known in 1778 that the bleaching of plants was due to the absence of light (Bonnet; Duhamel; Meese, "Journ. de Phys."). Chlorophyll is chiefly acted upon by yellow or red light. In 1854 Gardner recognized that the green leaves of plants decompose carbonic acid, and liberate oxygen, more readily under a yellow glass than under a blue glass. Deherain, and more especially Pfeffer ("Pogg. Ann.," 1872, p. 442), examined the photo-chemical action in question by means of leaves immersed in water. Measuring the oxygen set free, Pfeffer found that the following volumes of gas were liberated:—

In the red	25'4
„ orange	63'0
„ yellow	100'0
„ green	37'2
„ blue	22'1
„ indigo	13'5
„ violet	7'1

The development of gas does not seem to give altogether the amount of carbonic acid decomposed. Timivirazeff ("Compt. Rend.," vol. xciv, p. 1236), in his very exact spectrum researches, and by analysis, having insolated the leaves placed in an atmosphere charged with carbonic acid, found that the greatest decomposition of carbonic acid took place in the red between B and C; these rays are directly and very markedly absorbed by chlorophyll. In the orange, yellow, and green the quantity of carbonic acid decomposed diminishes, in the ultra-red there is no decomposition; on the other hand, carbonic acid is developed by respiration. Previously, Draper, Lommel (Pogg., vol. cxliii, p. 581), and Müller ("Fortsch.

Phys.," 1872, p. 146) confirmed the observations of Timivirazeff. The latter, however, first investigated the question. The greening of the mono- and decotyledons can be effected by all parts of the spectrum. The action of the red rays is the most energetic; the blue, the violet, and ultra-violet act but slowly. The rays so light, as well as the dark rays, reinforce the respiration of the plants. According to Wiesner ("Vienna Academie Ansieg.," 1876, p. 137), the ultra-violet appears without effect in this work. The rays belonging to the region of those absorbed by chlorophyll favour respiration. According to Krauss ("Fortsch. Phys.," 1870, p. 406) and Brillenin ("Comp. Rend.," 1870, p. 511), chlorophyll makes starch in plants merely by the action of light, and this much more in the red than in the blue. Famintzin had already shown experimentally that the production of starch in chlorophyll only took place in diffused yellow light (behind bichromate of potash), and not in diffused blue light (behind cupric oxide dissolved in ammonia), in which indeed the starch disappears.

Light is absolutely necessary for organic life, especially for the growth of plants (Radan, "La Lumière et les Climats;" Becquerel, "La Lumière," vol. ii, p. 235). In the light plants decompose carbonic acid from the air, giving up oxygen. It has long been known that the quantity of oxygen liberated by plants increases with the intensity of the light; that a cloudy sky diminishes it; and that darkness renders it *nil*. In the dark, plants breathe like animals; that is to say, they absorb oxygen, and emit carbonic acid. Fruits also breathe like animals. Light makes leaves green, and colours flowers. Without light no chlorophyll is formed; the green cones of the conifers, however, do not require light for their development.

THE SEEDS OF PLANTS are influenced by different kinds of light. According to Hunt, yellow, red, and green light are hurtful to germination; whilst blue light favours it; whilst in the after-development blue light acts less favourably than does yellow, red, and white light. Zantedeschi ("Compt. Rend.," 1817, p. 349) obtained more rapid germination under a green glass; then under violet. Yellow, orange, and red glasses had a less favourable action.

To these inexact and contradictory statements (because they

were obtained by means of coloured films) Poggiale, in 1817, opposed his researches with the pure spectrum. He found that the germination of plants was more rapidly effected in red than in green light; and more rapidly in the green than in the violet.

Many stems of flowers and trunks of trees bend towards the light: daily experience teaches that plants turn towards the light. Dr. Gardner, in 1814, was the first to study the details of this phenomenon by means of the spectrum. If seeds are allowed to germinate and grow for some days, they develop vertical stems several inches in length; if then they are exposed in such a manner as to receive the influence of the spectrum, they begin to curve. When placed in the other parts of the spectrum the stems turn towards the indigo; in the indigo they curve towards the incident rays. If taken into the dark they return to their vertical position ("Phot. Corr.," 1873, p. 71). The principal action takes place in the indigo, near G. Poggiale also remarked this ("Compt. Rend.," 1842 and 1844). The blue, violet, and ultra-violet rays alter the curvature of the stems of plants in retarding their growth.*

According to Böhm ("Wiener Anzeig.," 1874, p. 47), a light too feeble to give rise to chlorophyll produces heliotropic curvature. These observations are in favour of positive heliotropism—a fight for light.

Many plants have a sort of sleep; that is to say, the flowers close. They wake, according to Hoffmann (1850), more readily in blue or yellow light than they do in red or white light. The scent of some kinds of flowers is much more intense at night than in the day; similarly, as many animals rest during the day to wander at night, so many scented plants are inactive during the day. In the movements of leaves the least refrangible rays act as darkness, whilst the direction of

* See the action of light on plants, Sachs, "Botanique," 1874, p. 727. In particular, for the action of coloured light on plants, "Botanik Zeit.," 1865, where will be found publications on this subject. Bert ("Compt. Rend.," vol. lxxiii) thinks that all colours are hurtful to vegetation, and that white light alone is really favourable. According to this, horticulturists should do away with the employment of coloured glass in their houses for young plants. As to the influence of light on organic matter (vegetable or animal), see Foissac, "Météorologie," 1859, p. 65; and Wiesner, "Bull. de l'Acad. de Vienne."

the movement is determined by the blue, violet, and ultra-violet rays.

The action of the different coloured rays of the solar spectrum can be formulated as follows (Sachs, "Lehrbuch der Botanik," 1874, p. 709):—A mixture of rays of different refrangibility, of white solar light, and which appears to our eyes as variously coloured bands of the spectrum, has a physiological action on vegetation of such a character, that the chemical action depends principally on the mean or less refrangible rays (red, orange, yellow, and green); it is thus in the greening of chlorophyll, in the decomposition of carbonic acid, and in the formation of starch (sugar or fat) in chlorophyll.

On the other hand, the most refrangible rays, blue, violet, ultra-violet, have a preponderating influence on mechanical changes, so far as they depend completely on the light. It is these rays which have influence on the rapidity of growth, change the movement of protoplasm, give a determinate direction, and make the cellular tissue in organs of movement of many leaves to vary, as well as their composition.

INFLUENCE OF LIGHT ON ANIMAL LIFE.—Light has also considerable influence on animal life. Lavoisier, at the end of the eighteenth century ("Traité Élémentaire de Chimie"), wrote:—"Without light nature would be without life—dead, inanimate." I do not mention the modern fantastic writing, "Use in Medicine of the curative power of the Violet and Blue Light." On the contrary, the remark made by William Edwards in 1824 is important, that frogs' spawn placed in an opaque glass perish, whilst those placed in a transparent glass were regularly hatched. The hatching of perch is retarded in the dark. Many illnesses are due to too violent an action of light,—for example, sun-strokes; whilst others, from a want of light,—for example, scrofulous diseases.

Bécharde found ("Compt. Rend.," 1858, p. 441) that flies' eggs were hatched more rapidly under a blue or violet glass than under a white, red, yellow, or orange glass. Guarinoni believed he found a favourable influence of violet light on the silkworm. According to Salmi and Piacentini ("Fortsch. der Phys.," 1871, p. 463), animals give out most carbonic acid under yellow or green glass; these colours should favour

respiration. Moleschott stated in 1855 that frogs breathed more freely in daylight than they did in the dark. The sun browns the skin, reddens the blood, whilst the Esquimaux become pallid in their long winters; most probably blue or violet light is most effective in this case.

VISUAL PURPLE.—The visual purple discovered by Kuhne in the retina is bleached by light, but is coloured afterwards. It is very sensitive to the yellow-green, and little to the red rays; the sensitiveness is analogous to the absorption of colours. In the light this purple becomes yellow, absorbing principally the blue or violet, and thus decolorizing very rapidly by it.

It is known that different colours have a different effect on men and animals. Usually blue or violet rays appear to act the most on animal organisms, and the yellow and red rays on plants. Nevertheless, this grave question has been but little studied as yet.

CHAPTER XIV.

GENERAL EFFECT OF THE SPECTRUM.

WE have seen that light and the pure spectrum colours act sometimes by oxidation and sometimes by a reducing action. This variable phenomenon of oxidation and reduction, is it subject to fixed laws? Must one attribute to a certain kind of light of the spectrum an oxidizing action, and to another kind a reducing action? It is difficult to reply, in spite of all the preceding observations, to these questions. Chastaing has made the most complete study on the influence of coloured light on chemical phenomena, and more especially on those of oxidation. Since this interesting work is only found succinctly given in German extracts (Pogg., "Beib.," 1877, p. 517), I have taken the liberty to give some original details beyond those already described above.

Most of the experiments lasted days, weeks, and even months before Chastaing undertook to give the relative instead of the absolute numbers. A great number of experiments were made under coloured glasses, first examined by the spectroscope; in other cases he worked with the spectrum only.

White Light.—When white light acts on a binary metallic compound, its action is mostly reducing, like that of violet light; rarely oxidizing. In general it can be said that white light acts by reduction. The phenomena of oxidation are principally to be attributed to a secondary chemical action, or to a particular absorption of light.

Violet Light reduces the metallic combinations, and in less time than white light.

Green Light does not exercise any important action; it is feebly reducing. Green light is almost always mixed with a little yellow.

Red and Yellow Light.—At first sight these rays do not seem to act on metallic salts. In reality they have an inverse action to that of violet light.

To fix more exactly the oxidizing or reducing action of light, a comparative experiment was every time made in the dark. The value of the oxidation was determined by measuring the oxygen or by titration. During the determination of the absorption the substance was not in direct contact with mercury; it was also placed in a small flask with a flat bottom, and the air which was in the flask isolated by means of mercury. A quantity of mercury, proportional to the oxygen absorbed, entered the tube: by weighing the mercury, the volume of the gas was easily found. In other cases the quantity of oxidized matter was determined volumetrically.

The temperature should remain constant during these experiments, to prevent phenomena interfering with the proceedings. At a high temperature the oxidation is largely increased, and the influence of light unrecognizable; even variations of 5° to 6° C. have their effect. This was remarked above all for ferrous sulphate. In all experiments, then, the influence of temperature should be avoided.

Chastaing concluded from his researches on the combinations of manganese, chromium, and mercury (*see above*),—

- 1st. The chemical action of the spectrum on binary combinations and upon salts is double—reducing for one part of the spectrum and oxidizing for another. He established the photo-chemical action by opposite curves,—the first the curve of reduction as generally known, the second that of oxidation, whose existence is not attributable to a single peroxide or perchloride, &c., but also to all readily oxidizable bodies.
- 2nd. The reducing chemical action is much more pronounced than the oxidizing chemical action. The state of the sky causes oscillations in the intensity.
- 3rd. The green rays have a feeble chemical force, and act as the blue rays.
- 4th. It follows from the presence of these two opposite chemical actions that there ought to be a point in the spectrum where the chemical action of light

is *nil*. This neutral point is found between D and E.

Chastaing considers the formation of hydrochloric acid as a phenomenon of reduction (combination with hydrogen), and attributes the anomalies presented by silver iodide and sulphurous acid as due to a secondary chemical action.

For organic substances he arrives at the following conclusions :—

- 1st. The photo-chemical action exercised on organic bodies is oxidizing.
- 2nd. Its intensity varies with each body, but remains the same if oxidation in the dark is called 1, in the red 2, in the blue-violet = about 3.
- 3rd. At the commencement, the oxidizing action of the green is feeble; after that it increases, to become finally more intense than that shown in the red.

Mixtures of organic bodies, and of inorganic salts submitted to light, show a complicated decomposition. The effect is due to a conglomeration of simple actions. But as all reducing action furnishes oxygen in the nascent state, which in its turn acts by oxidation in other combinations, it follows that the oxidation provoked by light reduces itself by the presence of organic combinations which oxidize themselves strongly.

Chastaing deduces from his researches on mixtures of uranium nitrate or of ferric chloride with alcohol or ether, that several cases can present themselves.

- 1st. The red and yellow rays oxidize the organic substances less than the salts: the result is a reduction of the salt.
- 2nd. The red and yellow rays oxidize the organic substances as much as the salt; or
- 3rd. They oxidize more the first—that which causes a reduction of the salt.

In the study of fluorescent substances, very complicated facts are arrived at. Some of these, such as an alcoholic solution of tournsol, modify themselves possibly even under the influence of all the rays (*see higher*); others, on the con-

trary, like sulphate of quinine and turmeric, only under the influence of the rays provoking fluorescence. There is here a new molecular modification, as with quinine, or else an oxidation, as with turmeric. The total energy of the absorbed rays exciting fluorescence, do not serve further for fluorescence, but a portion of these same rays is utilized to realize a chemical action.

H. W. Vogel objects to the theoretical conclusions of Chastaing (Pogg., "Beib.," 1877, p. 681). First of all, he remarks that the facts of Chastaing are not exact in the case of chlorine and hydrogen. This, in effect, transforms itself into chemical combination under the influence of violet rays, and is not to be considered, with Chastaing, as a reducing action. The properties of silver salts are very contradictory. From the violet to the red, there is a reducing action (*see ante*), and only rarely oxidation takes place.

Again, the strongest decomposition of carbonic acid by plants (still a reducing action) takes place in the red (*see ante*). To the capital fact that certain rays impede the action of others—a fact which agrees with Chastaing's theory—Vogel's opposes others taken from the photography with silver salts. Thus, paper dyed with ultramarine or cobalt blue, which is less affected than white paper by the so-called oxidizing red rays, acts less energetically than this latter,—that is to say, in hindering oxidation. The same fact is presented by madder lake, which reflects many more red rays than cobalt paper, and besides presents as strong an action as ultramarine. Vogel concludes from the principal known facts on the action of light on organic bodies, that each kind of ray can also induce reducing as well as oxidizing action, according to the nature of the body absorbing these rays.

Colouring matters are most bleached by oxidation by the rays they absorb: thus not always by the violet rays.

In the actual state of our knowledge on the chemical action of coloured light, it is not possible to make exact general conclusions from a relatively few experimental researches. Many phenomena cannot be considered from one point of view, as the controversy between H. W. Vogel and Chastaing shows; and only when a large number of combinations are experimented with will it be possible to avoid contradictions.

But if it is not possible to find fixed rules; at the same time the greater part of the observations show—

- 1st. Every colour of light, from the violet to the red, as well as the invisible ultra-violet and infra-red rays, can exercise a chemical action.
- 2nd. The rays having a chemical effect on a body ought to be absorbed by that body; the chemical action of light and optical absorptions are intimately combined.
- 3rd. Every kind of light can act by oxidation or reduction, according to the nature of the body which is sensitive to the light.
- 4th. Although the oxidizing action of the red rays and the reducing action of the violet rays cannot be sharply separated, it can be said that in general red light acts ordinarily by oxidation in metallic combinations, and violet light by reduction.

Red light is seen sometimes to act by reduction on metallic combinations, notably in the latent action of light on salts of silver. Up till now, no positive oxidizing action has been met with by violet light on metallic compounds.* In the combinations of metalloids with them, violet or blue light seems to act most energetically, as, for instance, on chlorine and hydrogen, nitric acid, sulphurous acid, hydroiodic acid: sulphuretted hydrogen in water is, however, decomposed most rapidly by red light.

The action of light is in part oxidizing, in part reducing, according to the nature of the substance. In the most cases violet light has a very energetic and oxidizing action on organic compounds, chiefly when colourless. Colouring matter is strongly oxidized by the luminous rays which they absorb.

Altogether, in all cases the chemical action of coloured light obeys the law, that the rays having

[* We do not hold to this: the reversal of the violet end of the spectrum, &c., or AgI, by prolonged exposure is a case in point.—*Editor.*]

the most energetic action are also those which are most absorbed by the substances sensitive to light.

- 5th. Not only does the absorption of the luminous rays by the bodies themselves, but also the absorption of light by the substances mixed with them, play a considerable rôle in the chemical action of light. The sensitiveness to light of the first is found strongly augmented by the luminous rays which the latter absorb (optical sensitizers *).
- 6th. A substance mixed with a body sensitive to light, and which can combine chemically with the matter eliminated by light (oxygen, iodine, bromine, &c.), favours the decomposition by light. These bodies are given the name of chemical sensitizers.
- 7th. The manner in which it acts in presence of a coloured light varies considerably with the purity of the compound, according to its molecular state, eventually with the nature of the development of the latent image.
- 8th. The direct decomposition of a compound by the luminous rays do not go exactly with the luminous latent image.
- 9th. The action of the solar spectrum varies considerably with the state of the atmosphere, in such a manner that for the same state of the sun and sky, apparently pure, the chemical effect is rarely the same. It is also difficult to give the absolute figures relative to the chemical action of the colours of the spectrum.

A great part of the changes induced by the action of light are also produced by elevation of temperature. It is thus that many chlorides and metallic oxalates, in solution in alcohol or ether, are more or less reduced by the temperature of boiling; and amongst them, in the first place, are the organic salts of silver. Ferrous sulphate rapidly oxidizes in red light as in heat. Colouring matter bleaches not only in the air and by light, but also by heat. A temperature of 150° to

[* The reader will have gathered our objection to this term.—*Editor.*]

200° C. induces a combination of chlorine and hydrogen. In many cases, however, a high temperature cannot replace that of light. Silver chloride does not decompose even at red heat ; it is the same for the iodide and bromide of silver. The great resistance of this body, so easily decomposed by light, shows clearly that heat and light can act separately. Light, again, acts when the calorific rays are absorbed by means of proper appliances absorbing the heat,* as with a solution of alum, and not the light. It is to be remarked that it is principally the cold parts of the spectrum which give rise to chemical action, and not the warm parts. Thus the attempts of Rumford, Gay-Lussac, and Thénard (Gmelin, "Handbuch der Chem.," vol. v, p. 169) to explain the action of light by an elevation of temperature are not admissible. In many cases, it is true, an elevation of temperature increases the action of light.

[* By heat the author evidently means what is popularly and incorrectly called "radiant heat." It would have been better to have said in the line above,—“Light again acts when the rays of long-wave length are eliminated ;” and again,—“It is to be remarked that it is principally in the parts of the spectrum which possess least energy which give rise to chemical action, and not those parts which possess the most.”—*Editor.*]

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